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CHEMISTRY AND VISUAL IMPACT OF THE PLUMES FROM THE FOUR CORNERS POWER PLANT AND SAN MANUEL COPPER SMELTER

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16. ABSTRACT

This paper presents a study of the conversion of SO_2 to particulate sulfur in a Western power plant plume and in a Western copper smelter plume, the impact of these plumes on visibility, and the relative contributions of primary and secondary aerosols to this impact. For plume ages greater than 3 h, the rates of conversion in the power plant and smelter plumes were similar (0.4 to 0.8% h^{-1}) with the higher rate in the smelter plume. For very young plumes, the conversion rates differed substantially. The low conversion (0-0.1% h^{-1}) in the very young plume of the power plant appears to be related to the depletion of oxidant by nitrogen oxides. The very high conversion rate (2-4% h^{-1}) in the smelter plume with less than 1 h plume age was in part due to the absence of nitrogen oxides in the smelter plume. In the Four Corners region most of the particulate sulfur was in the form of ammonium sulfate during the sampling period. The data suggest that most but not all of the particulate sulfur in the San Manuel plume and background was in the form of sulfate.

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ABSTRACT

This paper presents a study of the conversion of SO_2 to particulate sulfur in a western power plant and in a western copper smelter plume, the impact of these plumes on visibility, and the relative contributions of primary and secondary aerosols to this impact. The conversion of SO_2 to particulate sulfur has been studied in some detail in order to determine its importance to the near source and long range visual impact of the plumes from the Four Corners power plant and San Manuel copper smelter. All measurements were made on clear days. It is shown that during this sampling for plume ages greater than 3 h, the rates of conversion both in the power plant and smelter plumes were similar (0.4 to 0.8% h^{-1}) with the higher rate in the smelter plume. The conversion mechanism most likely involved oxidation of SO_2 by OH radicals. The higher conversion rate at the San Manuel smelter may have been due to the high concentration of water vapor (8-10 mm Hg) relative to that in the Four Corners region (1-5 mm Hg) during the study. For very young plumes, the conversion rates differed substantially. The low conversion (0-0.1% h^{-1}) in the very young plume of the power plant appeared to be related to the depletion of oxidant by the nitrogen oxides. The very high conversion rate (2-4% h^{-1}) in the smelter plume with less than 1 h plume age was in part due to the lack of excess nitrogen oxides in the smelter plume. However, the fact that conversion was so much higher than that for the older plume suggests that some other mechanism such as heterogenous oxidation was taking place. In the Four Corners region most of the particulate sulfur was in the form of ammonium sulfate during the sampling period. The data suggest that most but not all of the particulate sulfur in the San Manuel plume and background was in the form of sulfate (no ammonium measurments were made in this region). Close to the smelter there was significant primary nonsulfate sulfur present. The particulate composition in the Four Corners power plant plume was shown to be consistent with flyash while that from the San Manuel copper smelter was consistent with copper ore. The major contribution to excess light extinction due to the plume at the Four Corners power plant and the San Manuel smelter is light scattering by primary particles. This accounts for about 90% of the excess extinction from 5 km to 10 km downwind and decreases to about 70% by 25 km to 30 km downwind. Light scattering by primary sulfate particles was found to contribute very little to the extinction in the Four Corners power plant plume: 2% of extinction at 5 and 25 km from the plant. In the San Manuel smelter plume, light scattering by primary sulfate particles contributed much more: 55% of extinction at 10 km and 22% at 35 km from the smelter. Light scattering by secondary sulfate particles makes a minor contribution to the plume excess extinction at Four Corners (2 to 5%) while at San Manuel it contributes ~7 to ~34%. The larger contribution in the smelter plume was due to higher conversion rates and the lack of NO_2 in the plume. Light absorption due to NO_2 does not contribute to the San Manuel plume excess extinction but makes a modest contribution to that of Four Corners increasing from 6 to 18% of the plume excess extinction from 5 km to 25 km downwind.

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1. INTRODUCTION

It is now generally recognized that haze is present in all parts of the continental United States even in the relatively pristine desert southwest. The US Environmental Protection Agency undertook Project VISTTA (Visibility Impairment Due to Sulfur Transport and Transformation in the Atmosphere) in order to study the haze in the southwest and to assess the contributions of various sources to visibility reduction.

The VISTTA program has been going on for several years. The October 1977 field program has been described earlier (Macias et al., 1979; Macias et al., 1980). The results from 1979 field studies are also documented (Richards et al., 1981; Macias et al., 1981; Hering et al., 1981; Bergstrom et al., 1981; Blumenthal et al., 1981). In this paper we discuss the results of the second VISTTA field program (fall of 1978) in which the plumes from a western coal-fired power plant and from a copper smelter were studied to determine the important components of the visibility-reducing-aerosol from these two sources. To determine the relative importance of primary and secondary pollutants to the extinction due to the plume, measurements of primary aerosol, of NO and NO_2 and of particulate sulfate and SO_2 were made under various meteorological conditions. These allowed estimates of the conversion of nitrogen and sulfur species under varying conditions. A low pressure impactor (LPI) with eight stages from 0.05 to 4 μm aerodynamic cutpoint was used to measure the size distribution of particulate sulfur in the air and on the ground. The light scattering due to sulfur was calculated from these data using Mie theory. Finally, scattering data and the elemental composition of the plume excess aerosol were used to analyze the relative impact of primary and secondary components of each source type on the visibility in the area near the source.

2. CONCLUSIONS

2.1. SULFUR DIOXIDE CONVERSION

1. The conversion of SO_2 to particulate sulfate in the Four Corners power plant plume and in the San Manuel copper smelter plume at ages greater than 1 h is consistent with homogeneous gas phase oxidation by OH radical.

   a) The conversion appears to depend on water vapor concentration, ozone concentration and UV radiation. These are all necessary for production of OH radical in the relatively unpolluted desert atmosphere by the reactions

$$O_3 \xrightarrow{h\nu} O(D^1) + O_2$$

$$O(D^1) + H_2O \longrightarrow OH.$$

   b) The rates of 0.4% h^{-1} for Four Corners on September 16, 1978 and 0.8% h^{-1} for San Manuel on September 27, 1978 were consistent with those calculated by Calvert et al. (1978) for the latitudes of Four Corners and San Manuel for a July day at noon of 0.8% h^{-1} and 0.94% h^{-1}.

   c) The lower rates near the Four Corners plant are most likely due to the depletion of O_3 by NO which is expected to decrease the OH concentration in the plume.

2. Conversion of SO_2 in the young (<1h) smelter plume under daylight conditions is possibly dominated by heterogenous conversion on primary particles.

   a) The large conversion rate of ~4% h^{-1} was seen only close to the stacks where SO_2 and particulate concentrations were high.

   b) Heterogenous oxidation could occur near the stacks at San Manuel and not at Four Corners (which has a higher primary particulate concentration) because of the lack of competition with NO for the oxidant, the higher concentrations of copper, iron, zinc and magnanese which may be catalytic to the conversion and the higher water vapor concentrations during the smelter plume measurements.

2.2. SULFUR SIZE DISTRIBUTION

1. In the Four Corners power plant plume, significant amounts of large diameter (> 2 μm) particles containing sulfur were measured in the plume both at 4 and 25 km downwind. The composition of these particles is indicative of flyash enriched in sulfur. Sulfur associated with fine particles (diameters between 0.1 and 2 μm) was seen in some plume samples. Very

small particle sulfur (< 0.1 μm aerodynamic diameter) was measured in large concentrations with ambient temperatures below 18° C both in sampling on the ground and from an airplane in the mixed layer. This very small particle mode sulfur was not present in samples taken at higher ambient temperatures.

2. In the background of the Four Corners power plant plume no significant concentration of large particle sulfur (d > 2 μm) was present either in ground based or aerial measurements. The aerodynamic sulfur mass median diameter from these background measurements was 0.2 μm which is in agreement with that found in other VISTTA measurements at Zilnez Mesa, AZ in 1979, and in Los Angeles, CA under dry conditions suggesting homogeneous gas phase oxidation (Hering and Friedlander, 1981).

2.3. ELEMENTAL COMPOSITION OF PLUMES

1. The particulate composition in the Four Corners power plant plume was shown to be consistent with flyash analyses from this plant. Sulfur was enriched relative to iron at increasing downwind distances from the plant indicating particulate sulfur formation in the plume.

2. The particulate composition in the San Manuel copper smelter plume was shown to be consistent with copper ore. Again enrichment relative to sulfur was seen as indicating particulate sulfur formed from SO_2 in the plume.

2.4. EXTINCTION BUDGET AND PLUME IMPACT

1. The major contribution to excess light extinction due to the plume at the Four Corners power plant and the San Manuel smelter is light scattering by primary particles. This accounts for about 90% of the excess extinction from 5 km to 10 km downwind and decreases to about 70% by 25 km to 30 km downwind.

2. Light scattering by primary sulfate particles was found to contribute very little to the extinction in the Four Corners power plant plume — 2% of extinction at 5 and 25 km from the plant. In the San Manuel smelter plume, light scattering by primary sulfate particles contributed much more — 55% of extinction at 10 km and 22% at 35 km from the smelter.

3. Light scattering by secondary sulfate particles makes a minor contribution to the plume excess extinction at Four Corners (2 to 5%) while at San Manuel it contriubtes 7 to 34%. The larger contribution in the smelter plume was due to higher conversion rates and the lack of NO_2 in the plume.

4. Light absorption due to NO_2 does not contribute to the San Manuel plume excess extinction but makes a modest contribution to that of Four Corners increasing from 6 to 18% of the plume excess extinction from 5 km to 25 km downwind.

3. PROGRAM DESCRIPTION

The 1978 VISTTA field program was carried out from September 12-28, 1978. This project complemented the 1977 measurements by studying in more detail plumes from a coal-fired power plant and a copper smelter in the Southwestern United States. Aircraft based sampling was carried out on twelve days as summarized in Table 1. The aircraft was equipped with instruments listed in Table 2 and with an inlet configuration shown schematically in Figure 1.

Five days were spent studying the plume and background of the Four Corners (NM) power plant located 30 km SW of Farmington (NM). The plant has five units with a maximum output of 2100 MW. During the study period the plant output varied from 900 to 2100 MW. The emissions during the study period were estimated to range from 182 to 384 tons/day of SO_2 (Nicholson, 1981). Trijonis (1979) has estimated the emission of 143 tons/day of NO_2 from the plant in 1975. The plume was studied at a number of downwind distances from 2 to 65 km with flight paths as shown in Figure 2.

The San Manuel (AZ) smelter plume was studied on two days with most useful data coming from the flights on September 27, 1978 at downwind distances of 10 to 90 km. Flight paths for this day are shown in Figure 3. The San Manuel smelter is located 50 km NNE of Tucson (AZ) and emitted an estimated 601 tons/day of SO_2 in 1978 (Larson and Billings, 1979).

The plume flight patterns were designed to provide a detailed characterization of the plume at discrete distances downwind from the source. Care was taken in all measurements to avoid plumes of nearby Stacks. This was not a serious problem because the plume of interest was well defined and separated from other plumes on all sampling days considered. Horizontal traverses at several elevations were generally made at each distance from the stacks. These traverses were in a direction normal to the plume and included sampling of the plume as well as background air on either side. Vertical spirals were made on some flights to determine vertical plume structure and background mixing height. Orbital flights within the plume of up to one hour were also carried out over fixed ground locations at each distance to gather impactor and filter samples loaded heavily enough for subsequent elemental and chemical analyses. Orbits upwind of the source were flown to collect background samples.

To supplement the aircraft measurements a number of ground based measurments were taken at two observation stations of the Arizona Public Service Company in the Four Corners area and at Mesa Verde National Park (Figure 4). The types of ground based measurements carried out are summarized in Table 3. There were also single theodolite pilot balloon

TABLE 1. VISTTA 78 PROGRAM SUMMARY MRI QUEENAIR

Date	Flight Objectives	Flight Times (MDT) start	stop	Flight Hours	Plume Sampling Distances (km)
9/12/78	Ferry - Los Angeles to Farmington	14:40	19:08	4.5	Regional
9/14/78	Four Corners power plant (NM) plume Traverses, orbits, spiral	6:50	11:30	4.7	20,40
9/15/78	Four Corners plume Traverses, orbits, spirals	10:17 16:00	14:00 20:05	3.7 4.1	5,25 5
9/16/78	Four Corners plume Orbits and spiral	7:49 11:55	11:35 12:55	3.8 1.0	2,12,34,55
9/18/78	Four Corners plume Traverses and spiral	6:31	8:15	1.7	20
9/20/78	Four Corners plume Traverses, orbits, spirals	7:54 16:00	13:37 17:38	5.7 1.5	20,40,65 0-5
9/21/78	Telephotometer sight path	8:23	12:15	3.9	Regional
	Ferry-Farmington (NM) to Tucson (AZ)	14:38	17:40	3.0	Regional
9/23/78	San Manuel copper smelter (AZ) plume Traverses, orbits, spiral	9:12	13:25	4.2	10
9/26/78	Regional sampling near smelters	11:43	20:33	8.8	Regional
9/27/78	San Manuel copper smelter plume Traverses, orbits	9:29	16:43	7.2	10,35,90, Bkg
9/28/78	Ferry - Tucson to Los Angeles	15:53	20:43	4.8	Regional

Table 2. Queen Air Instrumentation

Parameter	Sampler Manufacturer and Model	Analysis Technique	Particle Size Range (μm)	References
Aerosols Integral Size				
Light Scattering Coefficent	MRI 1569	Integrating	~0.1 - 1	b
Aerosol Charge Acceptance (ACA)	Washington University	Aerosol Charge Acceptance	~.01 - .1	c
Condensation Nuclei (CNC)	Environment One Rich 100	Light Attenuation	~.005 - .8	b
Aerosol Differential Size	Thermal Systems, Inc. 3030[a]	Aerosol Charger-Mobility Analysis	.0056 - 1	d
	Royco 218[a]	Optical Particle Counter with Multichannel Analyzer	0.56 - 18	e
	Knollenberg ASSP	Axial Scattering Spectrometer Probe	3 - 45	f
Aerosol Samples				
Total Sulfur	MRI TWOMASS Sampler/glass fiber filter	Flash Vaporization/ Flame Photometric Detection (FV-FPD)	<3	g,h
Sulfate and Nitrate	Bendix 240 Cyclone/Teflon impregnated glass fiber filters (RSP)	Ion Chromatography (IC)	<3	i
Total Mass	Bendix 240 Cyclone/Teflon impregnated glass fiber filters (RSP)	Gravimetric Weighing	<3	
Total Sulfur	Low Pressure Impactor (LPI)/ Vaseline coated stainless steel	Flash Vaporization/ Flame Photometric Detection (FV-FPD)	.05 - .075 .075 - .12 .12 - .26 .26 - .50 .50 - 1.0 1.0 - 2.0 2.0 - 4.0	j,k
Al - Pb	Lundgren Impactor/greased Mylar stages followed by Nucleopore after filter (LI)	Particle-Induced X-Ray Emission (PIXE) Some samples analyzed by X-ray Fluorescence (XRF)	<0.5 0.5 - 1.0 1.0 - 2.0 2.0 - 4.0 >4.0	l

Gases		
Sulfur Dioxide	Meloy 285	Flame Photometric
	Monitor Labs 8410	Chemiluminescence
	Monitor Labs 8440	Chemiluminescence
Other		
Dew Point Temperature	Cambridge Systems 137	
Turbulance		
Altitude Indicated Air speed	MRI Airborne Instrument Package	
Position-VOR DME	Aircraft Navigation System	
Visual Range	Optical Photography Telephotometer	
UV Radiation	Eppley Radiometer	Barrier-Layer Photocell

[a]Automatic bag sampling system for TSI 3030 and Royco 218; bagfill requires about 4 seconds, (Blumenthal et al., 1978)

[b]Sverdrup (1977)

[c]Husar et al. (1976)

[d]Liu and Pui (1975)

[e]Lieberman (1979)

[f]Jeck (1979)

[g]Macias and Husar (1976)

[h]Husar et al. (1975)

[i]Mulik et al. (1976)

[j]Hering et al. (1978 and 1979)

[k]Roberts and Friedlander (1976)

[l]Cahil (1975)

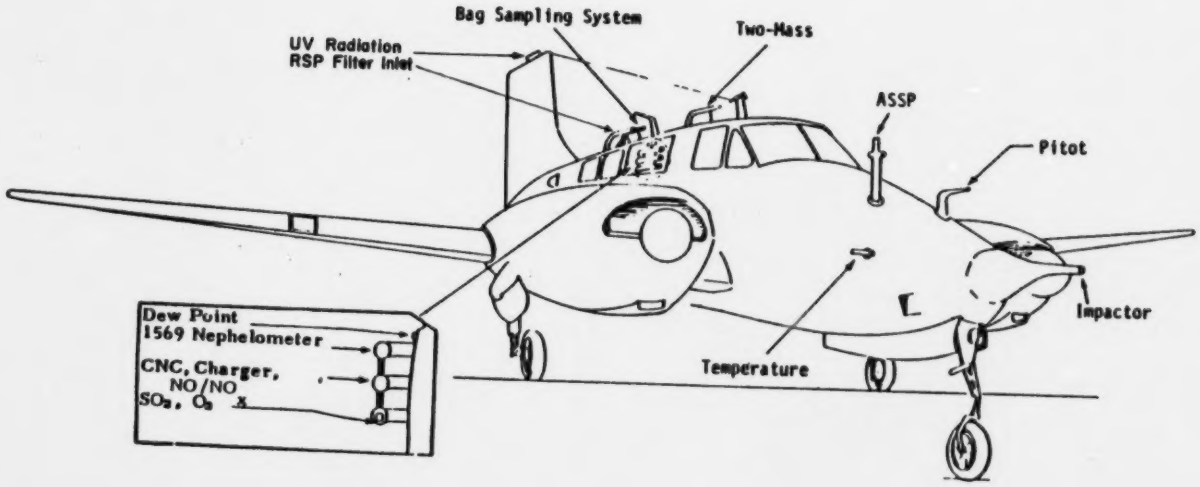


Figure 1. Schematic drawing of the Queen Air aircraft with inlets and instrumentation.

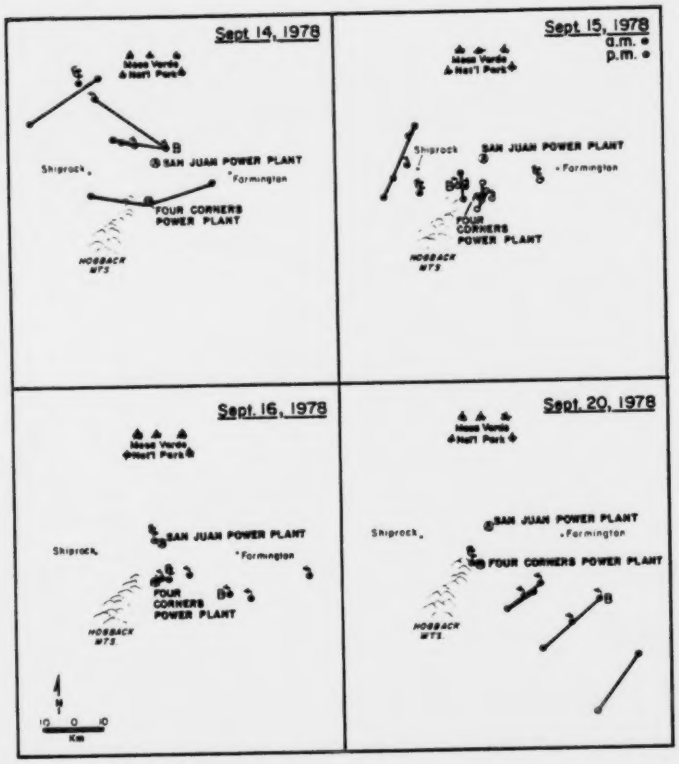


Figure 2. Flight paths for plume studies at the Four Corners power plant (NM). Traverses are indicated by —, orbits by ↻, and spirals by ↻. The background orbit is labeled with a B.

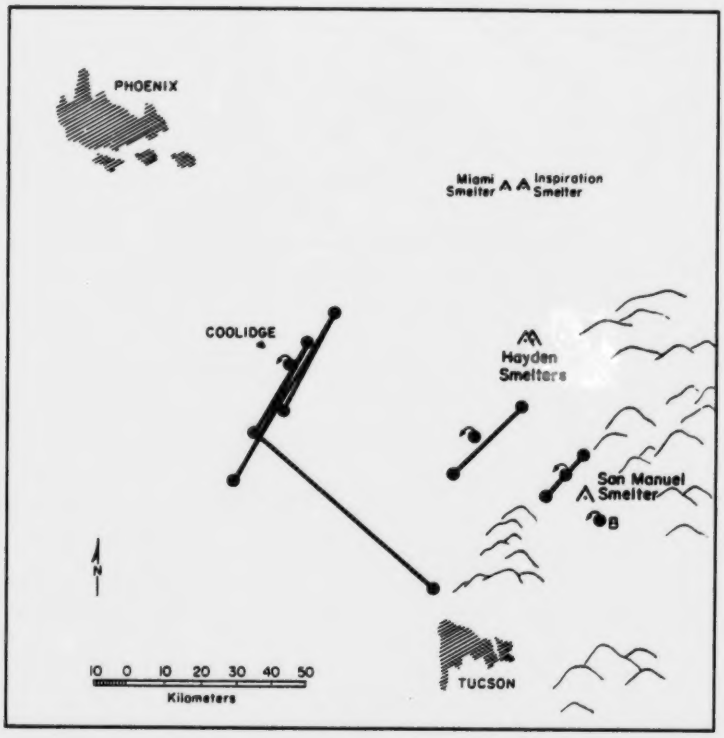


Figure 3. Flight paths for plume studies at the San Manuel smelter (AZ), September 27, 1978. Traverses are indicated by ⟷, orbits by ↻, and spirals by ↻. The background orbit is labeled with a B.

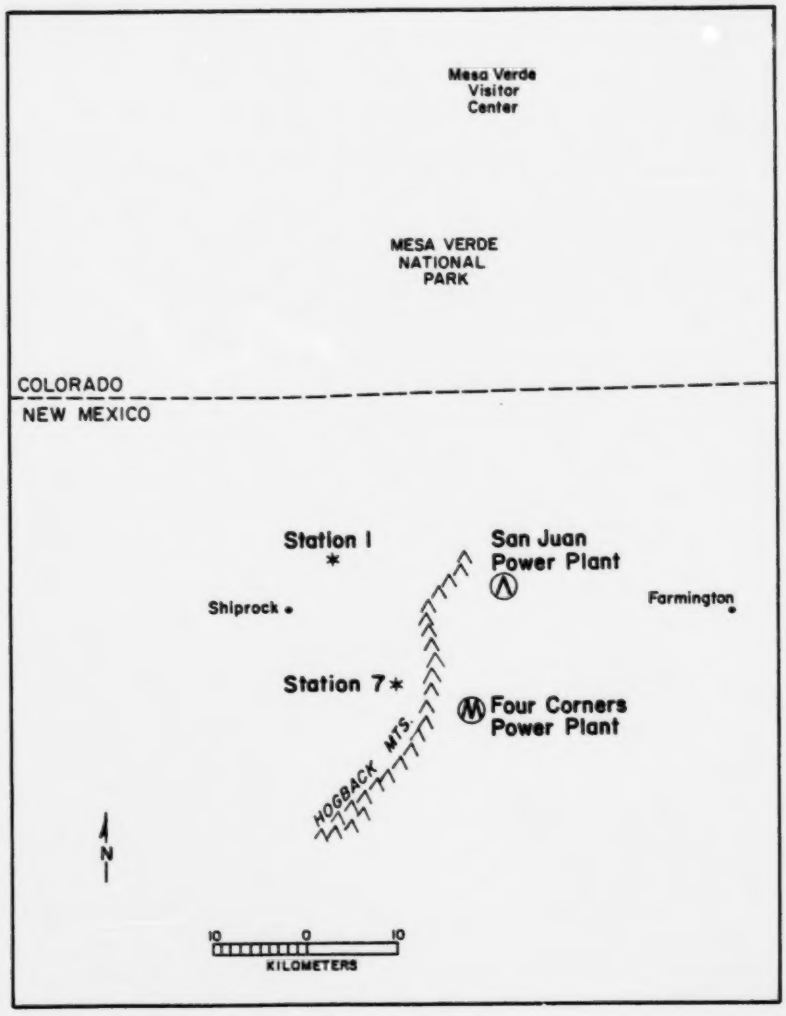


Figure 4. Ground sites near Four Corners power plant (NM) at observation station 1 and 7 of the Arizona Public Service Company and at the Visitor's Center at Mesa Verde National Park.

Table 3. Ground-Based Measurements Near Four Corners (NM)

Parameter	Sampler Manufacturer and Model	Analysis Technique	Particle Size Range (μm)	References	Location[a]
Light Scattering	MRI 1561	Integrating Nephelometer		b	1,7,MV
Size Distribution	Climet 201/ Royco 245	Optical Particle Counter with Multichannel Analyzer	0.3 - 4	c	1,7,MV
Condensation Nuclei	Environment One	Light Attenuation	~ .005 - .8	d	1,7
Carbon	TWOMASS (TM) Sampler/Quartz	Gamma Ray Analysis of Light Elements (GRALE)	<3	e,f	1,7
Ammonia	Tandem Filter	Colorimetric for NH_4^+		g	1,7
Total mass	AIHL Cyclone/ 3 m Teflon filter	Gravimetric Weighing	<3		1,7
	Modified Bendix 18 Cyclone/Nuclepore filter		<1	b	MV
Particulate Absorption	TWOMASS (TM) Sampler/Quartz	Reflectance	<3	e,h	1,7
	Modified Bendix 18 Cylcone/Nuclepore filter	Integrating Plate Method	<1	b	MV
Sulfate	AIHL Cyclone/ 3μm Teflon filter (AIHL)	Ion Chromatography (IC)	<3	i,l	1,7
	Low Pressure Impactor (LPI)/ Vaseline Coated stainless steel	Flash Vaporization/Flame Photometric Detection (FV-FPD)		j,l	1,7
Nitrate	AIHL Cyclone/ 3 μm Teflon filter	Ion Chromatography	<3	i,l	1,7
Visual Range	Telephotometer				

[a]Four Corner Sampling Station 1 = 1, Sampling Station 7 = 7; Mesa Verde Visitors Center = MV. All sampling locations are shown in Figure 4.

[b]Waggoner et al.

[c]Husar et al. (1976)

[d]Sverdrup (1977)

[e]Macias and Husar (1976)

[f]Macias et al. (1978 a,b)

[g]Richards and Johnson (1979)

[h]Delumyea et al. (1980)

[i]Mulik et al. (1976)

[j]Hering et al. (1978 and 1979)

[k]Roberts and Friedlander (1976)

[l]John and Reischl (1978)

(pibal) releases carried out at various times on every sampling day to determine wind direction and speed as a function of altitude in the Four Corners region and at Coolidge Airport near the San Manuel smelter.

4. RESULTS

Measurements were made to gain an understanding of the impact of the plumes on visibility at varying downwind distances. Plume orbits were used to obtain filter and impactor samples for determination of particulate concentrations and size distributions. Other parameters such as the scattering coefficients (b_{scat}), concentrations of SO_2, NO, NO_x and O_3 as well as meteorological data were also determined. The average values of these parameters for each plume and background orbit are given in Table 4 for the Four Corners power plant and in Table 5 for the San Manuel copper smelter.

4.1. SULFUR DIOXIDE CONVERSION

The average values of SO_2 and particulate sulfur (S_p) concentrations determined in orbital plume sampling along with other measured parameters which might affect the SO_2 conversion are given in Table 6. The release time and plume age were calculated from hourly pibal measurements near the power plant and smelter. The total UV radiation from plume release time to the median sampling time was determined from Figure 5 in which the mean UV radiation for a given pass is plotted against the median time (MST) of the pass. The NO_2/NO_x ratios in table 6 are listed as indicators of plume dispersion and availability of oxidant for the $SO_2 \rightarrow SO_4^=$ reaction and are, thus, not plume excess values.

The values of the particulate sulfur to gaseous sulfur ratio (S_p/S_g) versus plume age are plotted in Figure 6. Sulfur conversion rates determined from the slopes between two points from Figure 6 measured on the same day with plume releases within an hour of each other are listed in Table 6. The Four Corners data fall into a pattern of low conversion rates of 0.1 to 0.2% h^{-1} from 0.2 to 1 h plume age rising to a maximum of 0.4% h^{-1} from 3-5 h plume age. On the other hand the limited San Manuel smelter data indicate a maximum of 4% h^{-1} from 0.5 to 1 h plume age and a leveling off to 0.8% from 1 to 10 h plume age. The similar conversion rates of SO_2 in both the smelter and power plant plumes at ages greater than 3 h suggest a similar conversion mechanism is dominant in both plumes. In contrast to this the large difference in the plume sulfur conversion rates in the first hour indicates that there may be a different mechanism which dominates at less than 1 h plume age.

The sulfur particle to gas ratio (S_p/S_g) for the Four Corners power plant is plotted versus plume age again in Figure 7 where it is compared with the data from the Navajo Generating Station (NGS) reported by Richards et al. (1981). In this figure data from the same day have been connected where the plume release times are within 1 h of each other. The sulfur

Table 4. Average Parameters Measured During Plume Orbit Flights
Four Corners Power Plant[a]

Date	Time (MST)	Altitude (m msl)	Distance Downwind (km)	b_{scat} (10^{-6} m^{-1})	SO_2 (ppb)	O_3 (ppb)	NO (ppb)	NO_x (ppb)	$SO_4^{=}$ ($\mu g/m^3$)[b]	T[c] (°C)	d.p.[d] (°C)	UV ($W.m^{-2}$)	Condensation Nuclei Counts ($1000CM \cdot cm^3$)	Aerosol[e] Charge Acceptance
14 Sept. 78	7:19:14-7:34:11	1977±10	20	171±116	524±379	19±16	332±140	401±154	5.3	18.2	9.9	5±1	48±1	57±21
	7:40:15-8:20:20	2015±85	Bkg 20	22±4	5±6	54±6	5±3	11±7	1.2	18.1	9.6	8±2	44±1	29±2
	8:29:24-9:15:39	1936±164	Bkg 48	24±6	6±9	48±10	7±7	17±17	2.0	19.3	10.5	11±1	37±2	21±3
	9:48:46-10:19:10	1980±11	40	21±1	2±1	44±12	6±2	13±2	2.1	19.6	11.6	16±3	28±1	24±5
15 Sept. 78	9:45:13-10:07:30	1915±10	5	278±209	732±382[f]	16±9	860±339[f]	925±348[f]	10.9	17.5	-	14±6	-	-
	10:53:28-12:14:10	1883±38	25	42±12	28±14	40±6	16±6	31±10	3.3	19.5	-	18±4	-	-
	17:55:01-18:41:04	2019±49	5	53±37	120±100	35±17	85±44	108±54	3.7	21.4	-	1±3	-	-
	15:26:51 17:28:25	1918±18	Bkg	26±27	<2	62±7	7±4	9±6	2.4	22.9	-	7±4	-	-
16 Sept. 78	7:48:51 8:14:15	1888±17	2	217±126	590±362	14±2	514±257	590±278	6.4	17.6	.6	3±1	-	74±35
	8:28:36-8:48:34	1995±18	12	141±72	324±208	14±10	231±121	269±133	5.7	17.0	.6	5±1	-	40±10
	9:14:47-9:46:10	1989±16	34	49±15	81±34	21±6	43±19	74±24	4.2	17.1	.5	9±1	-	28±2
	10:03:28-10:35:01	1969±17	55	35±6	35±13	33±6	20±7	42±11	3.7	18.0	1.1	12±3	-	27±6
	10:55:00-11:55:00	1985±13	Bkg.	7±1	<2	51±3	5±2	6±2	1.7	19.8	1.8	15±4	-	15±7
20 Sept. 78	8:20:59-8:35:59	1879±13	20	177±66	254±104	13±10	181±75	238±97	4.0	6.0	-7.2	10±2	-	71±18
	8:47:20-9:19:20	1888±13	Bkg. 20	24±4	<2	48±2	<5	<5	1.1	6.6	-7.9	12±4	-	19±4
	10:45:00-11:05:06	1956±10	40	46±11	32±9	39±3	18±11	36 10	2.4	9.9	-10.7	18±3	-	30±8
	11:10:00-11:48:57	1969±47	Bkg. 40	21±3	<2	59±3	<5	6±7	1.8	10.6	-11.9	19±1	-	16±9

[a] The ± values given in this table are standard deviations from the averages of one minute values of the parameter over the orbit time.

[b] $SO_4^{=}$ concentrations from the RST/IC data; all values ±0.4 µg/sample or ~0.2 to 0.6 µg/m³.

[c] All values have standard deviation less than 1.

[d] All values have standard deviation less than 1.

[e] Relative units.

[f] The averages may be low since the maximum values went off scale for large portions of the orbit.

Table 5. Average Parameters Measured During Plume Orbit Flights
San Manuel Smelter[a]
September 27, 1978

Time (MST)	Altitude (m msl)	Distance Downwind (km)	b_{scat} (10^{-6} m^{-1})	SO_2 (ppb)	O_3 (ppb)	NO (ppb)	NO_x (ppb)	$SO_4^{=}$[b] (ug/m^3)	t[c] (°C)	d.p.[d] (°C)	UV (W/m^2)	Aerosol Charge Acceptance[e]
10:14:27-10:26:39	1524±13	12	287±79	376±88	58±3	< 5	7±2	38.2	20.1	8.9	17±3	161±20
11:33:12-11:53:11	1544±19	35	133±31	118±25	59±3	< 5	5±2	27.0	22.3	7.3	18±2	132±17
13:13:47-13:37:47	1195±21	90[f]	52±7	18±2	61±3	< 5	5±2	9.7	25.9	6.9	18±2	73±7
14:34:29-15:02:01	1232±18	90[f]	52±10	4±1	62±4	< 5	7±2		26.8	5.1	14±2	45±8
8:50:30-9:30:33	1372±17	Bkg.	36±3	< 1	56±3	< 5	8±2	7.0	19.8	9.5	13±2	11±2

[a] The ± values given on this table are standard deviations from the averages of one minute values of the parameter over the orbit time.

[b] $SO_4^{=}$ values from the RSP/IC data; all values good to ±0.4µg/sample or ∿ 0.2 to 0.6µg/m^3.

[c] t = temperature; all values have standard deviation less than 1.

[d] d.p. = dew point; all values have standard deviation less than 1.

[e] Relative units.

[f] One hour stop.

Table 6. Parameters related to $SO_2 \rightarrow SO_4^=$ conversion. Four Corners Power Plant and San Manuel Smelter, September, 1978.

Location/ Date	Distance Downwind (km)	Median Sampling Time (MST)	Release Time (MST)	Plume Age(t_A) (h)	$\int_0^{t_A} UVdt$ (W · h · m^{-2})	O_3 (ppb)	H_2O[a] (mm Hg)	$\frac{NO_2}{NO_X}$	Temp. (°C)	S_p[b] (μg/m^3)	S_g[c] (μg/m^3)	S_p/S_g (%)	Slope k_t (%/h)
Four Corners													
9/14/78	20	730	650	0.6	2.3	19	4.7	0.17	18.2	1.4	612	.23	
9/15/78	5	1000	810	0.8	10.4	16	-	.07	17.5	2.8	864	.32	0.25
	25	1130	830	3.0	39	40	-	.48	19.5	0.29	33	.87	
	5	1820	1805	0.2	0.14	35	-	.21	21.4	0.43	142	.30	
9/16/78	2	800	750	0.2	0.6	14	4.8	.13	17.6	1.6	696	.23	0.11
	12	840	730	1.2	2.4	14	4.9	.14	17.0	1.3	382	.34	0.26
	34	930	620	3.2	13.0	21	4.7	.42	17.1	0.83	96	.86	0.43
	55	1020	520	5.0	22.0	33	5.1	.52	18.0	0.67	41	1.63	
9/20/78	20	830	720	1.2	13.2	13	2.7	.24	6.0	0.97	300	.32	0.19
	40	1100	840	2.3	33	39	2.1	0.5	9.9	0.20	38	.53	
San Manuel													
9/27/78	12	1020	940	0.4	6.4	58	8.6	.51	20.1	10.3	444	2.3	3.7
	35	1140	1030	1.1	19.3	59	7.6	.33	22.3	6.7	138	4.9	
	90	1325	955	3.7	55	61	7.0	.28	25.9	0.9	13	6.9	.71
	90	1445	1040	4.1	69	62		.43	26.8				
				3.9	62								
10/4/77	60	855	355	5	∿18	-	10.0		26.0	3.0[d]	89	3.4	.82
	127	1050	050	10	∿46	-	9.8		28.3	2.7[d]	36	7.5	

[a] The H_2O vapor pressures determined from the temperature and dew point values given on Tables 4 and 5.

[b] S_p is the plume excess sulfur concentration from the RSP/IC data at 25°C and 1 atm.

[c] S_g is the plume excess average SO_2 concentration converted to μgS/m^3 at 25°C and at 1 atm.

[d] S_p for 1977 is from the TM/FVFPD data as reported by Macias et al. (1980a) with background averaged from regional flights. The LI/PIXE data yield S_p/S_g of 4.0 and 10.4 for 60 and 127 km respectively yielding $k_t = 1.3h^{-1}$.

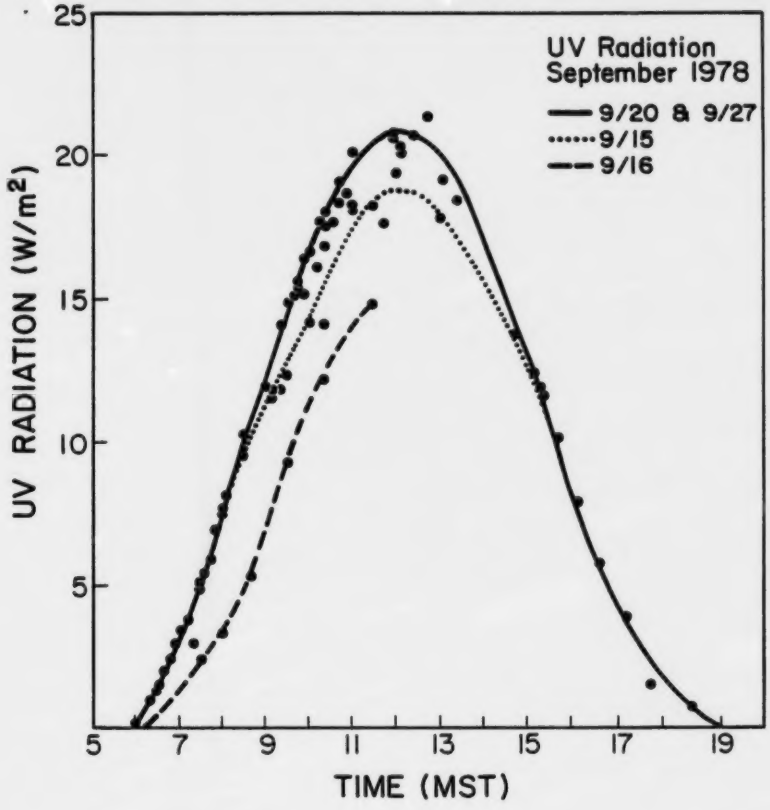


Figure 5. UV radiation (2956-3850 Å) determined during plume and background orbits and traverses in the Quenn Air aircraft, September 1978. Each point is the mean value plotted against the median time of the orbit or traverse.

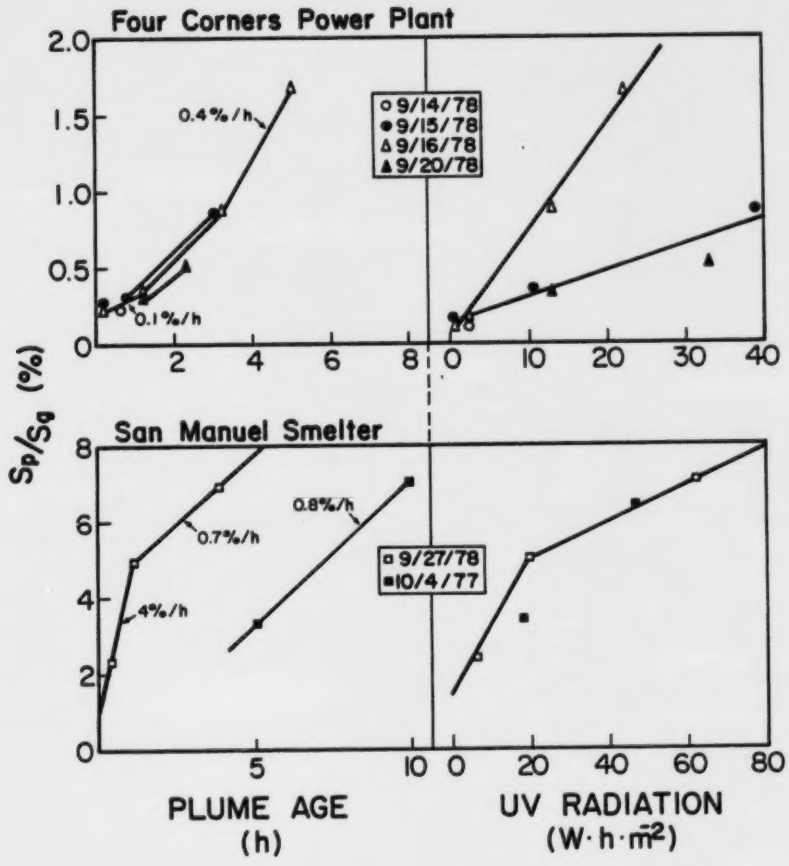


Figure 6. S_p/S_g vs. Plume Age and Total UV Radiation for the Four Corners power plant and San Manuel smelter, September 1978. Points on the same day with nearly the same plume release times (<1 h difference) have been connected and corresponding conversion rates calculated.

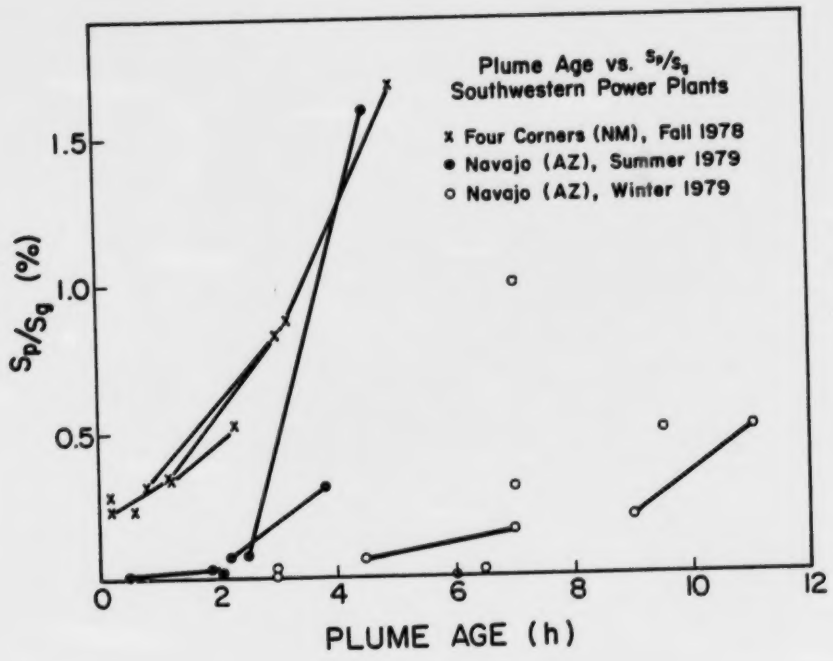


Figure 7. S_p/S_g vs. Plume Age for the Four Corners power plant in September 1978 (X) and Navajo power plant (AZ) in June-July (•) and December (o) 1979.

conversion rates in the Four Corners plume can be seen from the figure to be generally higher than the ratio in the NGS plume. Most measurements of the young NGS plume indicate conversion rates from less than 0.1% h^{-1} to 0.4% h^{-1}. From one pair of measurements at NGS (13 July 1979 between 840 and 1030 MST) a rate of 0.8% h^{-1} was calculated. One important difference between these two power plants is the greater amount of primary particulate sulfur emissions in the Four Corners plume estimated from the y-intercepts of Figures 6 and 7. This is confirmed by primary emission data where primary particulate sulfur was calculated to be 0.2% of total sulfur in the Four Corners plume as described in the next section. Richards et al. (1981) reported that the upper limit of the particle-to-gas sulfur ratio in the primary emissions at NGS was 0.02%.

4.2. PRIMARY PLUME PARTICULATE SULFUR EMISSIONS.

The intercepts of curves in Figure 6 can be used to determine the value of the ratio of primary plume particulate sulfur to gaseous sulfur $(S_p/S_g)_o$. This ratio is about 0.2% for Four Corners and 1% for the San Manuel smelter. For comparison with the aerial measurements, we have made estimates of the $(S_p/S_g)_o$ ratios at Four Corners from the daily generating capacities and load factors for the five units estimated from boiler heat rates (9.9 MBTU/MW-hr and 11.1 MBTU/MW-hr for units 4, 5 and 1, 2, 3 respectively), fuel heating value (8900 BTU/lb) and estimates of SO_2 and particulate removal by the precipitators on units 4 and 5 and the wet Venturi scrubbers on units 1, 2 and 3. It was assumed that the precipitators removed 95% of the particulate matter with 80% of the flyash carried over to the boiler and that 0.75% of the flyash was sulfur. For units 1, 2 and 3 with the Venturi scrubbers there was an assumed flyash emission of 0.05 lb/MBTU with 0.75% of the flyash as sulfur and an assumed 30% removal of SO_2. The ratio of total particulate sulfur from flyash to gaseous sulfur from SO_2 $(S_p/S_g)_o$ equals 0.6% to 0.7% calculated from the above assumptions of load factors and flyash composition at the Four Corners power plant. These values include particles of all sizes and therefore are higher than values from Figure 6 determined from aircraft plume sampling of particles with diameters less than 3 μm. This difference may be due in part to the presence of primary sulfur containing particles with diameters greater than 3 μm as well as to the uncertainty in the above assumptions. We have not calculated the $(S_p/S_g)_o$ for the San Manuel smelter because of the lack of reliable emissions data. A value of 1.4% was determined from primary emissions data ($d_p < 3$ μm) for a copper smelter in Utah (Eatough *et al.*, 1981) which is quite close to our value determined from the aerial data of Figure 6.

4.3. EFFECT OF SO_2 DEPOSITION ON CALCULATED CONVERSION RATES.

The values of S_p/S_g used in Figures 6 and 7 do not include a correction for SO_2 deposition because it is negligible for the plume age differences considered. To illustrate this we will consider the case for which

SO_2 deposition is calculated to be the greatest. That is the measurements between 34 km and 55 km at the Four Corners power plant on September 16, 1978 with a difference in plume age of 1.8 h. Between these passes the average solar radiation is 0.5 KW m^{-2} at a mixing height of 1500 m. Thus, the deposition velocity is estimated to be 1.04 cm s^{-1} (Gillani, et al., 1981). This results in a 4% deposition of SO_2 over the 1.8 h which changes the ratio of S_p/S_g from 1.63 to 1.50%, a relative error of 8%. Experimental uncertainties result in a relative error in conversion rates of similar magnitude. In fact applying Gillani's approximate correction for SO_2 deposition to all values of S_p/S_g has no significant effect on any of the conversion rates calculated here.

A more accurate formulation of the conversion rate expression would consider the ratio of secondary particulate sulfur to primary gaseous sulfur. The S_p/S_g ratios used here differ from the more exact expression by an amount less than the uncertainties in sulfur sampling and analysis.

4.4. THE RELATIONSHIP OF UV RADIATION TO SULFUR CONVERSION

In order to understand the effect of UV radiation on the conversion of SO_2 to particulate sulfur, the S_p/S_g values have also been plotted against UV radiation (2950-3850 A) for the Four Corners and San Manuel data in Figure 6. For Four Corners the data are separated into two groups. The group with the higher slope [0.09% $(W\ h\ m^{-2})^{-1}$] is from September 16, 1978 date. Two features in particular distinguish this day from the others in the Four Corners Plume Study: the plume was dispersed early in the morning beyond 12 km from the stack and the water vapor pressure was the highest. For the San Manuel smelter, the plot against UV radiation in Figure 6 shows both 1977 and 1978 data with plume ages >1 h nearly falling on the same curve with a slope of 0.13-0.16% $(W\ h\ m^{-2})^{-1}$, slightly greater than that for the Four Corners data set of September 16, 1978. The higher slope for data collected close to the smelter indicates that some factor other than or in addition to UV radiation is important to the conversion in the young smelter plumes, perhaps heterogenous conversion on the primary particulate emissions.

These data can be compared to data compiled by Wilson (1981) of particulate sulfur to total sulfur ratios and <u>total</u> solar radiation for twelve smelters and power plants in the U.S., Australia, and Canada. The only data from a western U.S. power plant in Wilson's complilation was the VISTTA data from the Navajo Genration Station (NGS) in June, July and December 1979 discussed in Section 4.1. Wilson concluded that all data except those from NGS fit reasonably well to a least squares line with slope 3.66% $(KW\ h\ m^{-2})^{-1}$ when S_p/S_T was plotted against the total solar radiation dose. The NGS data had a slope an order of magnitude lower [0.3% $(KW\ h\ m^{-2})^{-1}$]. The data from the present study can be compared to this by converting the measured UV radiation to total solar radiation (total radiation = UV radiation x 20, estimated from 1979 VISTTA UV and total solar radiation data). This comparison indicates that the data from San Manuel [slope 4-5% $(KW\ h\ m^{-2})^{-1}$] and from Four Corners on September 16, 1978 [slope 3% (KW h

$m^{-2})^{-1}$] agree with the main body of data in Wilson's review. The data from the other days at Four Corners, however, are much lower. This is similar to the NGS results when the greater primary emissions at Four Corners are taken into consideration. Thus, the data with greater dispersion and also higher water vapor content from September 16, 1978 had conversion rates comparable to eastern U.S. power plants while those on the other days had conversion rates comparable to those at NGS in June, July and December, 1979.

4.5. RELATIONSHIP BETWEEN NO_2/NO_x, AVAILABLE OXIDANT RATIOS, AND SULFUR CONVERSION.

We expect that SO_2 will compete with NO for oxidant species if the plume is oxidant limited and that the faster nitrogen reactions will be favored. This competition does exist in the Four Corner and Navajo plumes as shown in Figure 8. There we plot the particulate to gaseous sulfur ratio (S_p/S_g), an indication of SO_2 conversion, against the NO_2/NO_x ratio, an indicator of NO oxidation. Figure 8 shows that an increase in S_p/S_g due to secondary particulate sulfur formation appears only at relatively high NO_2/NO_x ratios (low NO concentrations). It should be noted that the data from the two power plants have similar functional forms but a large offset is apparent. This is partly due to a zero problem in the Four Corners NO and NO_x measurements. However, this is not likely to be the major reason for the difference in the data for the two plants. One possibility is the greater water vapor concentrations during the Four Corners sampling period yielding greater concentrations of OH at lower relative O_3 concentrations.

In the San Manuel smelter plume no measurable NO_x above background was observed as shown in Figure 9. This was also seen in passes near smelters during regional flights and is consistent with other VISTTA measurements (Macias *et al.*, 1979; Macias *et al.*, 1980). Variability in NO_x emissions from different smelters is suggested from the work of Small *et al.* (1981) who report very low (but measureable) plume excess NO_x at 8 km downwind of an unidentified Arizona copper smelter.

The lack of NO in the smelter emissions provides an interesting test of the idea that sulfur conversion will be higher at lower relative NO concentrations. The similarity in the conversion rates for the smelter at plume ages greater than 1 h and for the power plant plumes where the NO_2/NO_x values are large agrees with this hypothesis.

4.6. SULFUR CONVERSION MECHANISMS

We have shown that UV radiation, water vapor, background oxidant concentrations and dispersion all play some role in sulfur conversion although more data are needed to quantify the effects of these variables. These are consistent with the mechanism of SO_2 oxidation by OH radicals. Crutzen and Fishman (1977) suggest that the primary source of OH in relatively unpolluted air is from the following reactions

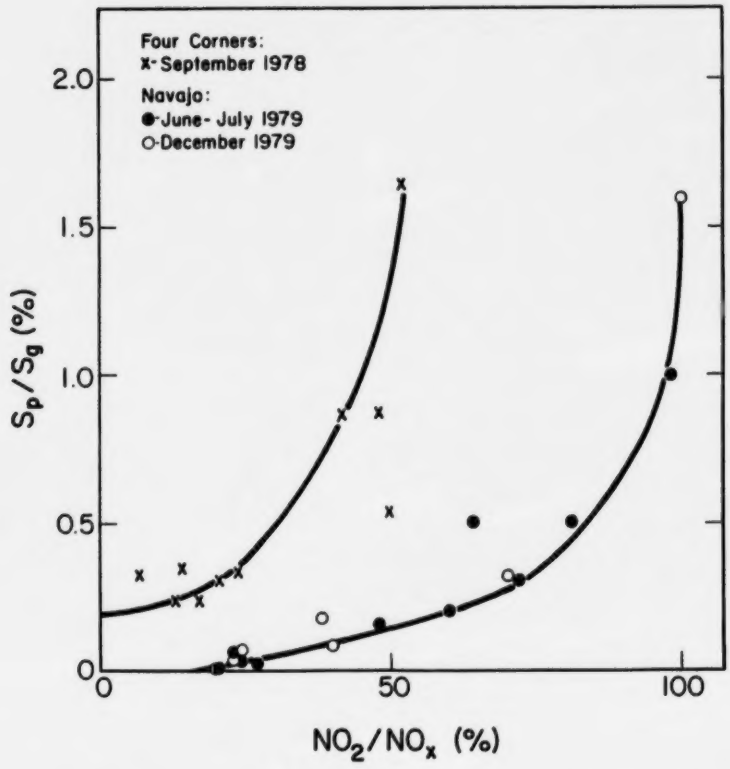


Figure 8. S_p/S_g vs. NO_2/NO_x for Four Corners power plant in September 1978 and Navajo power plant in June-July and December 1979.

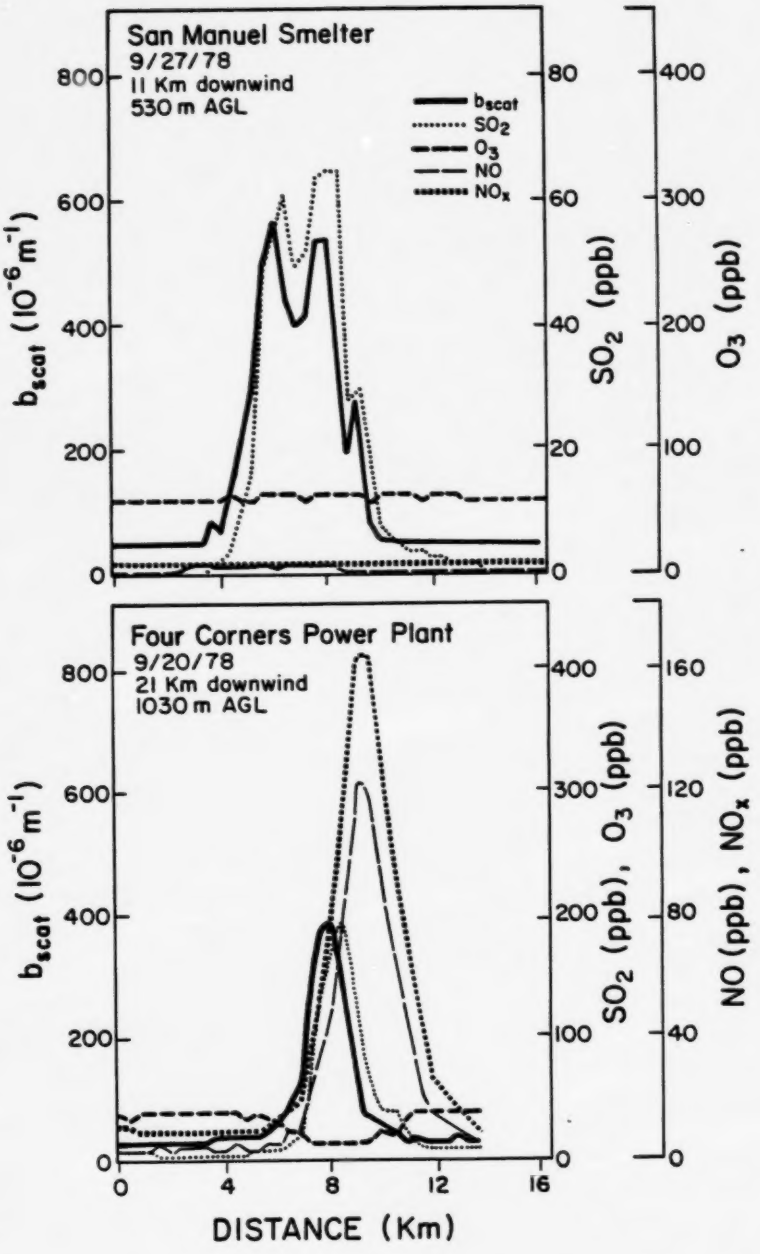


Figure 9. Traverses of the Four Corners power plant and San Manuel copper smelter showing the lack of plume excess NO and NO_x in the smelter plume.

$$O_3 \xrightarrow{h\nu} O(D^1) + O_2 \qquad (1)$$

$$O(D^1) + H_2O \longrightarrow 2OH \; . \qquad (2)$$

Background ozone and UV radiation (3000-3200 Å) are important for the production of $O(D^1)$ from equation (1) while water vapor is important through reaction (2). Comparison of water vapor pressures and conversion rates (Table 6) suggests that the lower conversion rates determined for the Navajo Generating Station plume relative to the Four Corners and San Manuel plumes may be due to the lower water vapor pressures during the NGS measurements (generally well below 3 mm Hg).

Calvert et al. (1978) predict oxidation rates of SO_2 by OH and HO_2 for noon on an average July day of 0.8% h^{-1} at 37° N latitude (Four Corners area) and 0.95% h^{-1} at 32° N latitude (San Manuel area). Our values of 0.4% h^{-1} at Four Corners and 0.8% h^{-1} at San Manuel are somewhat lower than the Calvert prediction as expected for September sunlight conditions. This supports the idea that the OH mechanism of SO_2 conversion to particulate sulfur is taking place in the power plant and the copper smelter plumes at >3 h plume age.

The extremely low SO_2 conversion in the Four Corners plume near the plant is probably due to the much faster oxidation of the NO and NO_2 which depletes the available oxidizing agents (O_3, OH, etc.). On the other hand, in the San Manuel smelter plume where NO and NO_2 values are at background levels, the conversion rate is highest near the sack, more than twice the rate further out. This suggest some other reaction path such as heterogeneous conversion. Although the total particulate concentration in the smelter plume is less than that of the power plant, the higher relative humidities and absence of competing NO oxidation reactions near the stacks where SO_2 concentrations are high suggests the likelihood of heterogeneous oxidation of SO_2 on the surface of the particulate emissions. Also, the elements (Fe, Zn, Mn and Cu) which are known to catalyze heterogeneous reactions (Williamson, 1973; Eatough, 1981) are present in relatively high concentrations in the smelter plume close to the stack.

4.7. NITROGEN CHEMISTRY IN THE POWER PLANT PLUME.

The concentration of gaseous nitrogen compounds and ozone for the various plume and background orbits at the Four Corners power plant are given in Table 7. Here Δ indicates the difference between plume and background concentrations. The data are consistent with the generally accepted photostationary steady state model (White, 1977; Peters and Richards, 1977). In this model the emitted NO reacts with the background ozone as rapidly as the gases are mixed

$$NO + O_3 \longrightarrow NO_2 + O_2 \quad (k_3)$$

while during daylight hours when the UV radiation is high the reverse reaction

Table 7. Comparison of Plume Excess NO_2 with O_3 Deficits Measured During Plume Orbits at Four Corners Power Plant (NM), September 1978.

Date	Distance Downwind (km)	Average Gas Concentration (ppb)				$\Delta NO_2+\Delta O_3$ [a] (ppb)	$\frac{\Delta NO_2+\Delta O_3}{\Delta NO_x}$ [b]
		NO_x	NO	NO_2	O_3		
14 Sept.	20	401	332	69	19	28	.07
	bkg	11	5	6	54		
15 Sept.	5 (AM)	925[c]	860[c]	65	16	29[d]	.03
	25	31	16	15	40	3[d]	.14
	5 (PM)	108	85	23	35	-6	-.06
	bkg	9	7	2	62		
16 Sept.	2	590[c]	514[c]	76	14	38	.07
	12	269	231	38	14	0	.00
	34	74	43	31	21	0	.00
	55	42	20	22	33	3	.08
	bkg	6	5	1	51		
20 Sept.	20	238	181	57	13	20	.08
	bkg	<2	<1	1	48		
	40	36	18	18	39	-5	-.17
	bkg	6	<3	3	59		

[a] $\Delta NO_2 = NO_2(\text{plume}) - NO_2(\text{bkg})$; $\Delta O_3 = O_3(\text{plume}) - O_3(\text{bkg})$.

[b] Positve $\frac{\Delta NO_2+\Delta O_3}{\Delta NO_x}$ indicates ratio of primary NO_2 to NO_x emissions near plant (White, 1977).

[c] NO, NO_x off scale during large portions of orbit so that averages may be low.

[d] Background O_3 for these orbits taken as 50 ppb $\pm$ 5 from traverses at nearly the same time since background orbit was flown in late afternoon.

$$NO_2 + O_2 \xrightarrow{h\nu} NO + O_3 \quad (k_4)$$

also takes place rapidly leading to a photostationary steady state cycle. These coupled reactions lead to the conservation of the sum of NO_2 plus O_3. This conservation relationship can be tested with our data using the ratio $(\Delta NO_2 + \Delta O_3)/\Delta NO_x$ given in the last column of Table 7. The values of this ratio near the plant range from 0.04 to 0.09. While fluctuations are likely due to experimental uncertainties, negative values may be related to HNO_3 production (Richards et al., 1981). The photostationary steady state reactions are not the only ones involving O_3, NO and NO_2, but the invariance of the ratio indicates that they are the most important.

4.8. AEROSOL ELEMENTAL COMPOSITION IN PLUMES.

The chemical composition of both the power plant and smelter plume aerosol was determined from samples collected by the modified Lundgren Impactor (LI) on the nose of the aircraft and analyzed by particle-induced x ray emission (PIXE) at the Crocker Nuclear Laboratory, Davis, CA. Because there is significant particle bounce onto the Nuclepore final filter (discussed in the Appendix) all stages were summed in this work to yield an elemental composition for particles of all sizes. These are listed in Table 8 for both power plant and smelter plumes at approximately 10 and 35 km downwind.

There are obvious differences between the two plumes at the same downwind distances which may be useful in determining the contribution of each type of source to the regional haze. The power plant always has larger concentrations of Al, Si, Ti and V while the smelter always has higher concentrations of S, K, Cr, Cu, Sn and Pb. This is consistent with the earlier VISTTA results from the San Manuel (AZ) smelter and Mohave (NM) power plant plumes in 1977 (Macias et al., 1979) and is related to the composition of the primary coal or ore.

That the plume aerosol composition is indeed related to the primary material is shown in Figures 10 and 11. Here the elemental enrichment factors are plotted using iron as a standard relative to the reference primary material (flyash for the power plant and copper ore for the smelter) [EF = (X/Fe)/(X/Fe) reference]. The enrichment factors relative to the earth's crust are also shown for comparison. A value of 1 for the enrichment factor indicates that the element is present in the abudnance of the reference material. Due to uncertainties in the data for both reference and plume concentrations, all values between 0.5 and 2 are taken to indicate no enrichment or depletion.

The data are most convincing for the power plant where the flyash analysis was done at the plant for a large number of samples from two of the units at Four Corners (Exxon Research, 1974). All elements fall within reasonable agreement with abundances in the flyash except sulfur at 34 km

Table 8. Plume Excess Elemental Concentrations in the Four Corners Power Plant and San Manuel Smelter Plumes, ng/m^3

	12 km	10 km	34 km	35 km
	Four Corners	San Manuel	Four Corners	San Manuel
Al	23186	3034	5037	115
Si	27766	10169	8177	4869
S	974	19046	411	6810
K	1329	1997	201	1280
Ca	2674	1876	562	857
Ti	749	30	213	29
V	472	*	698	*
Cr	391	561	5	470
Mn	52	21	1	296
Fe	4221	2016	852	651
Ni	24	28	9	*
Cu	48	1206	*	274
Zn	82	550	3	84
Se	*	25	5	*
Br	*	29	*	*
Pb	15	1339	*	178
Hg	65	*	*	*
Pt	143	*	9	*
Hg	120	*	*	*

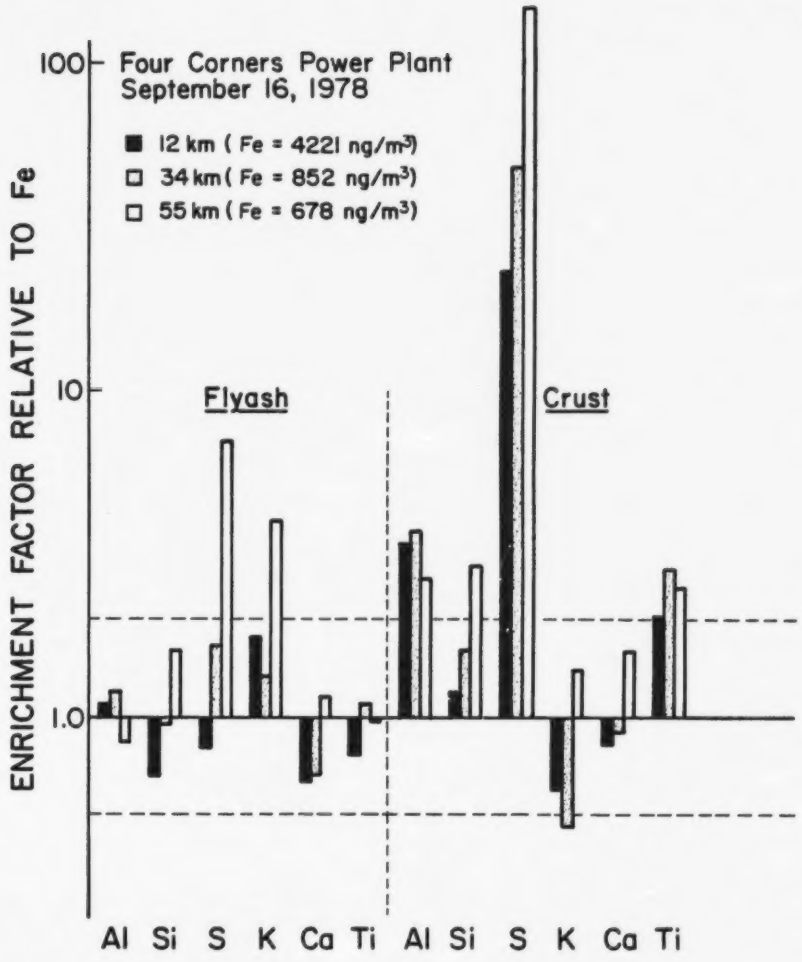

Four Corners Power Plant
September 16, 1978
12 km (Fe = 4221 ng/m³)
34 km (Fe = 852 ng/m³)
55 km (Fe = 678 ng/m³)
ENRICHMENT FACTOR RELATIVE TO Fe
100
10
1.0
Flyash
Crust
Al Si S K Ca Ti Al Si S K Ca Ti

Figure 10. Enrichment factors relative to Fe with flyash (Exxon Research, 1974) and earth's crust (Graedel, 1978) as reference materials. Four Corners power plant, September 16, 1978.

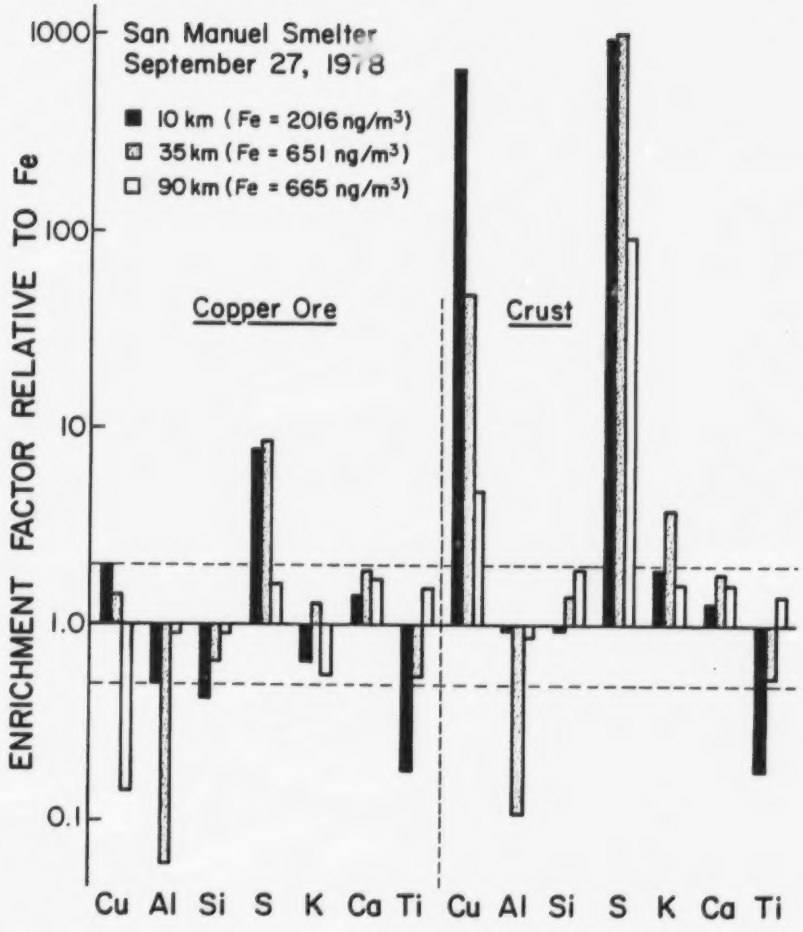


Figure 11. Enrichment factors relative to Fe with copper ore (Butts, 1954) and earth's crust (Graedel, 1978) as reference materials. San Manuel smelter September 27, 1978.

and 55 km downwind which is likely due to sulfate production in the plume and potassium at 55 km downwind which may be a result of vegatative burning near this orbit (Macias et al., 1981).

For the smelter, only sulfur shows enrichment relative to copper ore while Al, Si, and Ti show depletion for the 10 and 35 km orbits and Cu for the 90 km oribit. The data for the copper ore composition were taken from Butts (1954) and are a combination of data from the Ajo and San Manuel smelters because the San Manuel data were incomplete. Data taken from Germani et al. (1981) show depletions of S, Al, Si, K, Ca and Ti and enrichment of Cu to Fe in the precipitator dust relative to the copper ore for another Arizona copper smelter.

4.9. PARTICULATE SULFUR SIZE DISTRIBUTIONS.

Sulfur size distributions in the Four Corners region were determined from low pressure impactor samples in the air on September 15 and 20, 1978 and on the ground from September 15 to 21, 1978. The data from the aircraft included four plume samples and one background sample. Forty samples were taken on the ground. The samples taken during the highest and lowest SO_2 episodes are plotted in Figure 12 along with the data taken in the aircraft on September 15, 1978. For the ground data, it is assumed that the high SO_2 concentrations are related to a plume while the low SO_2 concentrations represent background aerosol.

A trimodal sulfur size distribution with an ultrafine aerosol peak at 0.09 μm, a fine aerosol peak at 0.9 μm and coarse aerosol peak at 9 μm was seen in aerial plume measurements close to the Four Corners power plant (5 km) on the morning of September 15, 1978. The ultrafine mode was also present in morning ground based plume measurements at 3 km and 25 km from the stacks. The ultrafine mode was not present in late afternoon aerial plume measurements when temperatures were 10-20° C higher. This small particle mode might be due to condensation of sulfuric acid vapor into droplets.

The average ratio of coarse particle sulfur (dp > 2 μm) to total gaseous sulfur in the plume at 5 km was 0.08% which can be used as an indication of primary particulate sulfur from the flyash. No significant particle sulfur concentrations were observed on the ground because of the low cutpoint of the cyclone used.

The sulfur concentration associated with particles of aerodynamic diameter > 1 μm was quite low in all background measurements. The aerodynamic mass mean particle size in the background was about 0.24 μm (the Stokes mass mean diameter was 0.10 - 0.15 μm). This is in agreement with the values from Zilnez Mesa (AZ) in June-July 1979 of about 0.2 μm aerodynamic diameter (Macias et al., 1981) except during an incursion of pollutants from Southern California (d = 0.3-0.4 μm). The 0.2 μm aerodynamic mass mean diameter is consistent with measurements by Hering and Friedlander (1981b) for homogeneous dry sulfate formation in Los Angeles CA.

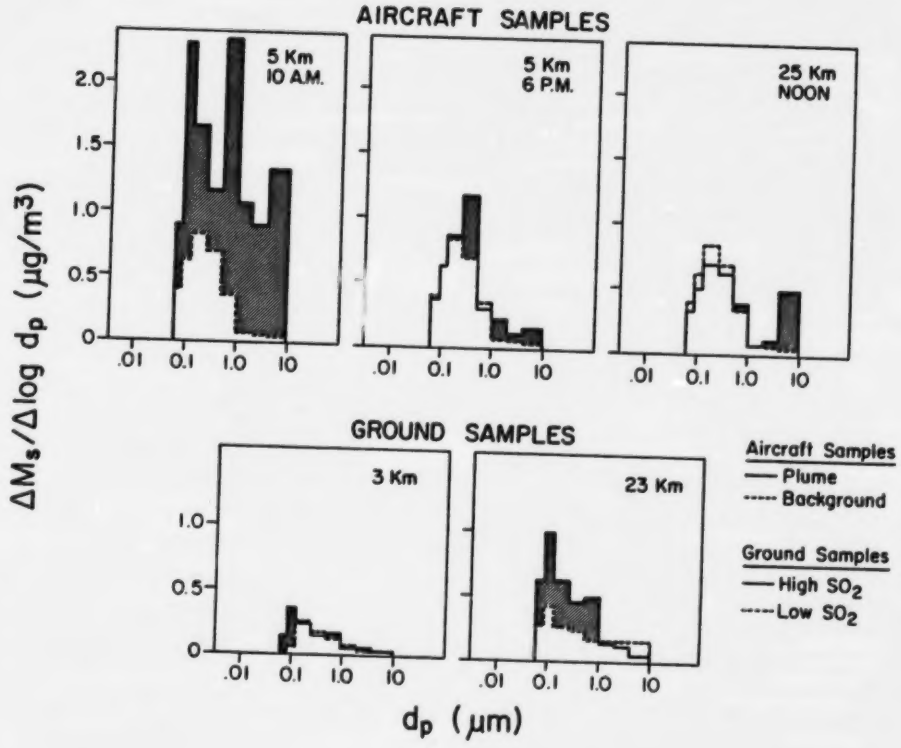


Figure 12. Sulfur size distributions from the LPI/FVFPD data, Four Corners power plant, September 1978. For the aircraft data, the background was measured at 4 P.M. on September 15, 1978. Aerodynamic diameters are plotted.

4.10. CHEMICAL COMPOSITION OF SULFUR.

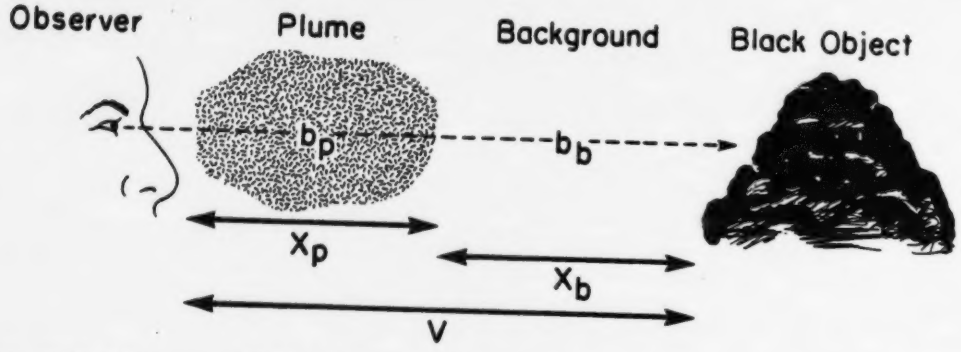
In the Four Corners plume and in the background, the sulfur appears to be in the form of ammonium sulfate. That the sulfur was in the form of water soluble sulfate is indicated by the excellent agreement between the total sulfur expressed as sulfate values determined by the RSP/IC method (slope = 1.09, intercept = 0.42 μg sulfate/m^3, correlation coeffiencent = 0.99, χ^2 = 0.23) (see Appendix for details). Ammonium ion concentrations were determined only for the ground site sampling. For the samples on which ammonium, sulfate, and nitrate ion concentrations were determined. The average concentrations were 14 nmoles sulfate/m^3, 34 nmoles ammonium/m^3, and 2 nmoles/m^3 of nitrate. These balance to within the sampling errors, indicating that at the ground site near the Four Corners power plant sulfur was in the form of ammonium sulfate. At the San Manuel copper smelter, most of the sulfur apperas to be in the form of water soluble sulfate except close to the plant where large primary sulfur particles (>4μm) make a significant contribution (see Appendix for details). This is in agreement with the data of Eatough et al. (1981) who found significant nonsulfate sulfur close to the stacks of Utah copper smelters. No ammonium data are available for the San Manuel copper smelter.

4.11. FINE PARTICLE SILICON.

The fine particle (d_p < 1 μm) silicon concentrations determined from the LI/PIXE data both for the regional and plume flights for the 1978 VISTTA programs are much higher than for the 1977 and 1979 data. Cahill (1981) has suggested that the Nuclepore final filters used in the 1978 VISTTA programs had unusually large and variable silicon blank values. This is supported by the fact that XRF analysis of these filters yielded negative silicon values for some filters when a standard blank was used. It is also likely that part of the fine particle silicon concentration is due to particle bounce to the final filter. The presence of significant particle bounce is indicated by comparison with EAA-OPC size distribution measurements and by the fact that the large particle silicon concentrations (d_p > 4 μm) are also higher for 1978 than 1977 and 1979. The Four Corners power plant, (studied in 1978) has 10 to 20 times the particulate emissions of the Mohave (studied in 1977) and Navajo (studied in 1979) plants. These particulate emissions are flyash which is 50% SiO_2 as shown in Section 4.8. Thus, it seems reasonable that the plume and background orbits for the Four Corners power plant would have larger total SiO_2 concentrations and more significant particle bounce. The coarse particle silicon concentrations for the San Manuel smelter in both 1977 and 1978 are comparable while the fine particle silicon is extremely large in 1978 measurements. This suggests that the blank problem may be important. Because of the uncertainty in the blank value for these data, no firm statement can be made about the concentration of fine particle silicon measured in this study.

4.12. VISUAL PLUME IMPACT.

The impact of a plume on visibility can be estimated by comparing the visual range with the plume present to the visual range through the background without the plume as described by Macias et al. (1980). The parameters used in this semi-quantitative calculation are shown in the schematic diagram below.



The subscripts p and b indicate plume and background parameters, respectively. The light extinction coefficient in the plume (b_p) includes the background contribution.

The visual range (V) is defined as "the distance, under daylight conditions, at which the apparent contrast between a specified type of target and its background becomes just equal to the threshold contrast of an observer" (Huschke, 1959). For the following analysis, the target is assumed to be a black object viewed against the horizon sky, and the threshold contrast of a typical observer (0.02) is used (Middleton, 1952). In this case, the visual range is given by

$$V = \frac{-\ln 0.02}{\overline{b_{ext}}} = \frac{3.9}{\overline{b_{ext}}} ,$$

where $\overline{b_{ext}}$ is the average extinction coefficient along the sight path. This equation assumes uniform illumination along the sight path and neglects multiple scattering.

In order to calculate the plume impact, one must have a good estimate of the components of the extinction coefficient. The nephelometer determines the scattering coefficient for particles less than 2 μm in diameter (Sverdrup, 1977) plus the Rayleigh scattering of gaseous aerosols. We have reasonable values of absorption due to gases from the NO_2 determinations. We do not have particle absorption values or values of scattering from particles with diameters greater than 2 μm but from other work we expect these values will be small (< 25% of total extinction due to particles) (Macias et al., 1981).

The equation for the visual range can be rewritten, $Vb_{ext} = 3.9$. For the case depicted above of a plume imbedded in background air, the

corresponding equation is $X_p b_p + X_b b_b = 3.9$, where b_p and b_b are the average extinction coefficients in the background and plume, respectively, and X_p is the measured plume width. The quantity $X_p b_p$ is the optical depth of the plume (τ_p)

$$\tau_p = \int b_p(x)\, dx,$$

which we shall approximate by $\overline{X_p b_p}$ using data in Tables 9 and 10. The visual range looking through the plume is calculated using the equation

$$V = X_p + X_b = X_p + \frac{3.9 + \tau_p}{b_b}$$

The visual range and plume optics calculations are summarized in Table 10.

The visual range through the copper smelter plume is reduced at 12 km downwind of the stack from 105 km in the background to 42 km with the plume present (60 percent reduction). The visibility reduction decreases farther downwind of the plant. For example at 90 km downwind, the visual range is 92 km with the plume present (13 percent visibility reduction relative to the background). The impact of the power plant is greatest when the plume is well defined in early morning and decreases at farther downwind distances. The impact was greatest on September 14, 1978, the only day when all five units were in operation during the VISTTA study. The reduction in visibility is significantly greater (51%) at 20 km downwind on the 14th when the load was ~2100 MW than at 25 km downwind on the 20th (35% when the load was 1200 MW). Although there may have been some overlap with the San Juan plume on September 14 since the plume was headed directly north, the additional effect on visibility should have been small because the San Juan output is scrubbed and is much smaller than the Four Corners plant - 700 MW (Miller, 1976) vs. 2170 MW (Trijonis, 1979).

4.13 EXTINCTION BUDGET.

Estimates are given in Table 9 for the contribution to extinction of fine particle ($d_p < 3$ μm) and coarse particle ($d_p > 3$ μm) scattering (b_{sp}), Rayleigh scattering (b_{rg}) and absorbtion due to NO_2 (b_{ag}) in the two plumes studied. Absorption due to particles (b_{ap}) was neglected in these calculations because no measurements were available. It can be seen that for both plumes, fine particle scattering was the most significant contributor to the extinction coefficient.

In the Four Corners plume extinction due to absorption by NO_2 was never more than twice that due to Rayleigh scattering. While the sulfate contribution to b_{sp} increased from 5 to 25 km, the sulfate percentage contribution to b_{ext} decreased due to an increase in b_{ag} from NO_2. The plume excess contribution of $(NH_4)_2SO_4$ (assuming all sulfur is in this form as described in section 4.10) to the total mass for the 4 orbits of September

Table 9. Contributions to the Extinction Coefficient. Four Corners Power Plant and San Manuel Smelter, September 1978.

	Neph. b_{sp} (10^{-6} m^{-1})	> 3μm[a] b_{sp}	b_{rg}	b_{ag}	$b_{ext.}$[c]	(b_{sp}/b_{ext}) Total (%)	b_{rg}/b_{ext} (%)	b_{ag}/b_{ext} (%)	($SO_4^=$)[d] b_{sp}/b_{ext} (%)
Four Corners									
20	159	54	12	21	246	86	5	9	-
5 (AM)	266	89	12	23	381	93	3	5	5
25	30	10	12	5	57	70	21	9	2
5 (PM)	41	14	12	8	75	73	16	11	5
2	211	74	12	25	322	88	4	8	-
12	130	83	12	13	227	94	5	6	-
34	37	15	12	10	86	74	14	12	-
55	23	8	12	7	50	62	24	14	-
20	165	58	12	19	254	88	5	7	-
40	34	12	12	6	64	72	19	9	-
San Manuel									
10	275	3	12	1	290	96	4	<1	-
35	121	1	12	<1	134	91	9	<1	-
90	40	0.4	12	<1	52	78	22	<1	-

[a] b_{sp} (d_p>3μm) estimated from Mie calculations to be ~0.33 b_{sp} (nephelometer) for the Four Corners power plant and 0.01 b_{sp}(nephelometer) for the San Manuel copper smelter.

[b] From NO_2 concentrations (Table 6) and extinction coefficients at 5500A° (Hodkinson, 1966).

[c] $b_{ext}=b_{sp} + b_{rg}$. No values for b_{ap} were measured.

[d] From Mie calculations using LPI/FVFPD data.

Table 10. Plume Impact Data. Four Corners Power Plant and San Manuel Smelter, September 1978.

Date	Distance Downwind (km)	Plume Width (km)	b_p ($10^{-6}m^{-1}$)[a]	b_b ($10^{-6}m^{-1}$)[b]	Plume Optical Depth (τ)	Plume Opacity ($1-e^{-\tau}$)	Visual Range (km)		Reduction Visual Range (%)
							With Plume Present	Background Only	
Four Corners									
September 14	20	9	246	22	2.2	.89	86	177	51
September 15	5 (AM)	4	399	26	1.6	.80	92	150	38
	25	10	57	26	0.57	.43	138	150	8
	5 (PM)	5	75	26	0.38	.31	140	150	6
September 20	20	6	254	24	1.5	.78	106	163	35
	40	9	64	21	.58	.44	167	186	10
San Manuel									
Septeuber 27	12	9	296	37	2.7	0.93	42	105	60
	35	15	134	37	2.0	0.87	66	105	37
	90	30	54	37	1.6	0.80	92	105	13

[a] b_{ext} in the plume from Table 9.

[b] b_{scat} from Tables 4 and 5.

15, 1978 corresponded exactly to the contribution of $(NH_4)_2SO_4$ to the extinction coefficient.

In the smelter plume the contribution of sulfate to the total LI/PIXE mass ranged from 63% near the plant to 56% at 35 km downwind. This decrease is likely due in part to fallout of large particle sulfur. It must be remembered that much of the sulfur present in the smelter plume was primary.

An estimate of the contribution of the secondary sulfate to the extinction for each plume was made using the conversion rates and values of (S_p/S_g) discussed earlier. The results of such an analysis are shown in Figure 13 for Four Corners on September 15, 1978 and San Manuel for September 27, 1978. It can be seen that for the power plant while NO_2 is more important than $(NH_4)_2SO_4$ in reducing visibility out to 25 km, scattering by primary particles is most important, ranging from 90% at 5 km from the plant to 75% at 25 km downwind. The total primary particulate contributions in the smelter plume are about the same as the power plant but scattering by primary sulfate is much greater. Scattering by secondary sulfate is much more significant in the smelter plume than the power plant plume even close to the stack and increases greatly by 34 km.

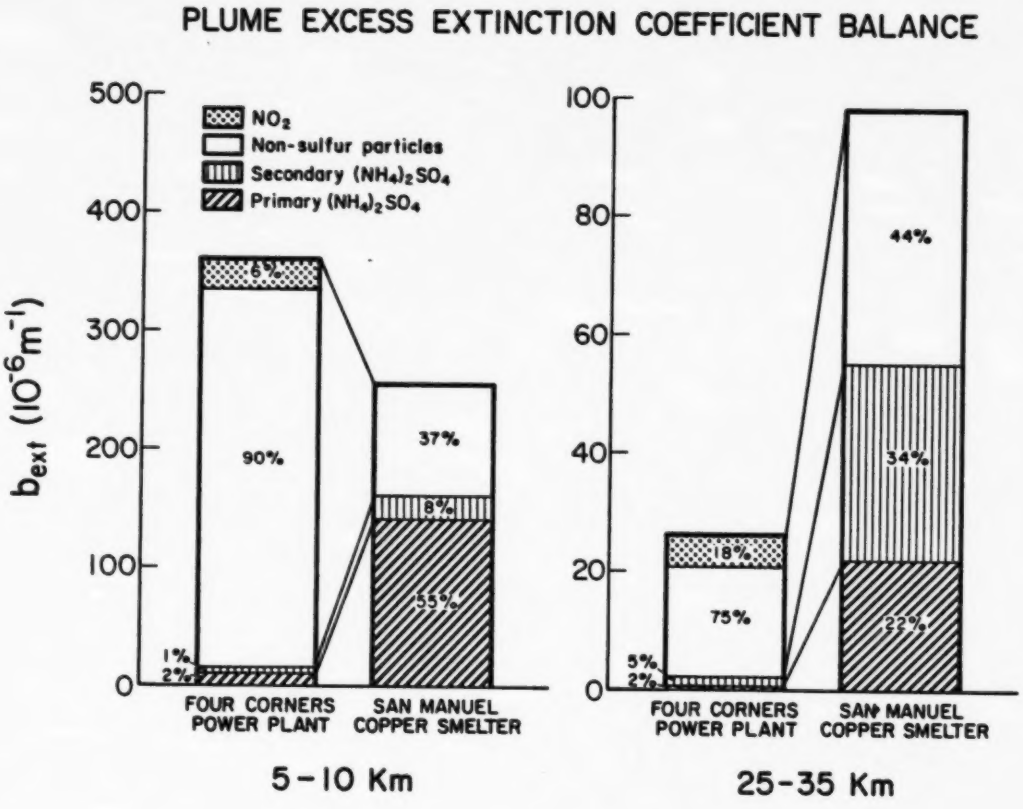


Figure 13. Contributions to the plume excess extinction coefficient for the Four Corners (NM) power plant and San Manuel (AZ) copper smelter. The Four Corners data are from the morning 5 km and 25 km orbits on September 15, 1978. The San Manuel data are from the 10 and 35 km orbits on September 27, 1978. All sulfur is assumed to be in the form of $(NH_4)_2 SO_4$.

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APPENDIX - DATA INTERCOMPARISON

1. PARTICULATE SULFUR CONCENTRATION.

In the VISTTA program of September 1978, sulfur concentrations in the plume and background were determined by four different samplers and analyzed by five different techniques. These are summarized and all abbreviations are explained in Tables 2 and 3 for the aircraft and ground data, respectively. All sulfur data are summarized in Tables A1, A2 and A3. Comparisons of these for the total data set including measurements in the Four Corners power plant plume, in the San Manuel Copper smelter plume and in the Southwest region are shown in Figure A1.

Figures Ala and Alc compare the ion chromatographic (IC) sulfate values and low pressure impactor (LPI) total sulfur values (assumed to be sulfate) with both samplers following the AIHL cyclone on the ground and the RSP cyclone in the aircraft. The excellent agreement between these data sets suggests that the particulate sulfur in the Four Corners region is mostly in the form of water soluble sulfate. This is consistent with the results at Zilnez Mesa (AZ) in June-July 1979 (Macias et al., 1981).

The agreement between the other sampler analysis technqiue combinations and the RSP/IC for the total data set is less good as can be seen in Figure Ala. The correlation coeficients are very good but the slope for the Lundgren impactor (LI)/Particle Induced X-ray Emission (PIXE) data is quite high while that for the Twomass (TM)/flash vaporization flame photometric detection (FVFPD) is quite low. The high slope and large negative intercept for the LI/PIXE data is largely due to the data point from the 10 km smelter orbit where one observes large concentrations of particles with aerodynamic diameters greater than 4 μm. These large particles would be collected with the LI but most would be removed by the RSP cyclone. A slope near 1 is obtained when this point is deleted. That light loadings on the filters may also be a cause for disagreement among the data sets is indicated by the lower correlation for the lightly loaded regional background samples. This can be seen also in the comparison of the several final filters analyzed by both PIXE and x-ray fluorescence (XRF) (Table A3). The heavily loaded smelter plume filters show excellent agreement between the PIXE and XRF values while the lightly loaded regional filters show very large differences. Because of this problem with lightly loaded samples, the LI/PIXE data were not used for sulfur values for most analyses. These data, however, were useful in showing the presence of very large sulfur particles in the San Manuel smelter plume. The LI/PIXE data were not useful for determing size distributions because of significant particle bounce to the final filter. This can be seen in Figure A2 in which the LPI/FVFPD and LI/PIXE sulfur size distributions and the EAA-OPC and LI/PIXE total size distributions are compared.

Table A1. Sulfur Data from the Ground Sites. VISTTA Field Program, September 1978. All data at NTP.

	LPI/FVFPD[a]		AIHL/IC[b]	
Location	Sample #	$SO_4^{=}$ ($\mu g/m^3$)	Sample #	$SO_4^{=}$ ($\mu g/m^3$)
1	-	1.39	138	1.39
7	1-3	1.93	142	.95
7	4-13	1.54	150	1.26
7	14-24	1.40	134	1.39
7	25-28	1.30	135	0.81

[a] Sum of all 8 stages with AIHL cyclone in front of LPI sampler. Each value here is the average of the samples listed and is adjusted to agree with AIHL/IC sampling times.

[b] Used blank of 1.36 µg $SO_4^{=}$/filter. The AIHL cyclone has a 50% aerodynamic cutpoint <3µm.

Table A2. Sulfate Data from Aircraft Sampling. VISTTA Field Program, September 1978.

Date	Location	Tape	LI/PIXE[a]		RSF/IC[b]		TH/FVFPD[c]		LPI/FVFPD[d]	
			Sample#/Slide #	$SO_4^=$ (μg/m³)	Sample#	$SO_4^=$ (μg/m³)	Sample#	$SO_4^=$ (μg/m³)	Sample #	$SO_4^=$ (μg/m³)
September 12	Ferry—L.A. to Farmington	571	A1/-	-	296060	0.61	023	0.51	-	-
			-	-	-	-	024	0.87	-	-
			-	-	-	-	025	0.00	-	-
			A2/-	-	296070	0.63	026	0.74	-	-
			-	-	-	-	027	1.03	-	-
September 14	Four Corners Power Plant Plume Study	572	A3/-	-	296080	0.00	030	0.18	-	-
			A4/-	-	296090	2.37*	031	0.00	-	-
			A5/-	-	296100	5.33	032	1.32	-	-
			A6/-	-	296110	1.24	033	0.59	-	-
			A7/-	-	296120	1.99	034	0.74	-	-
			-	-	-	-	035	0.40	-	-
			A8/-	-	296130	2.07	036	0.76	-	-
September 15	Four Corners Plume Study	574	B1/3	10.9	296150	10.46	-	-	1	11.8
			B2/4	4.2	296160	3.09	-	-	2	3.3
		575	B3/5	2.7	296170	2.27	044	1.61	3	3.3
			B4/6	4.3	296180	3.50	045	1.11	4	4.3
September 16	Four Corners Plume Study	576	B5/7	10.3	296190	6.36	047	2.40	-	-
			B6/8	*	296200	5.69	048	3.18	-	-
			B7/9	*	296210	4.24	050	3.50	-	-
			B8/10	7.1	296220	3.66	051	2.08	-	-
			B9/11	3.9	296230	1.68	053	1.56	-	-
			B10/12b	*	-	-	-	-	-	-
September 20	Four Corners Plume Study	579	C1/-	-	296240	3.68	100	1.24	-	-
			C2/13	7.5	296250	3.97	101	1.33	-	-
			C3/14	*	296270	1.13	102	1.04	-	-
			C4/-	-	296260	1.09	103	1.08	-	-
		579A	C5/15	*	296290	2.41	104	0.75	-	-
		(580)	C6/16	1.2	296280	1.79	105	0.55	-	-
			C7/-	-	-	-	106	1.93	-	-
		581	C8/17	3.5	296310	3.98	107	2.01	5	3.5
			C9/18	*	296300	2.98	108	2.42	-	-
September 21	Telephotometer Sight Path	582	C10/-	-	296320	1.38	111	0.63	-	-
			C11/-	-	-	-	112	1.30	-	-
			C12/19	*	-	-	113	0.60	-	-
			-	-	296330	1.49	114	0.70	-	-
			-	-	-	-	115	1.62	-	-
	Ferry-Farmington to Tucson	583	D1/-	-	296340	2.48	116	1.60	-	-
			D2/-	-	296350	*	117	2.53	-	-
			D3/-	-	296360	*	118	0.81	-	-
			-	-	-	-	119	2.25	-	-

(continued)

Table A2. (continued)

Date	Location	Tape	LI/PIXE[a]		RSP/IC[b]		TH/FVFPD[c]		LPI/FVFPD[d]	
			Sample#/Slide #	$SO_4^=$(ug/m^3)	Sample#	$SO_4^=$(ug/m^3)	Sample#	$SO_4^=$(ug/m^3)	Sample #	$SO_4^=$(ug/m^3)
September 23	San Manuel Smelter Plume	040	D4/-	-	296370	-	130	-	-	-
			D5/-	-	296380	-	136	-	-	-
September 26	Regional	041	E1/20	5.2	296390	2.91	144	1.68	-	-
			E2/21	*	296400	2.48	145	0.85	-	-
			E3/22	3.2	296410	1.56	147	0.79	-	-
			E4/23	1.5	296420	0.48	148	0.30	-	-
			E5/24	5.3	296430	1.24	149	0.38	-	-
			E6/25	4.1	296440	2.69	150	0.76	-	-
September 27	San Manuel Smelter Plume	042	E7/26	4.7	296450	6.99	153	1.42	-	-
			-	-	-	-	154	6.33	-	-
			E8/27	61.8	296460	38.23	155	19.09	-	-
			-	-	-	-	156	5.64	-	-
			E9/28	25.1	296470	27.00	157	12.32	-	-
			-	-	-	-	158	1.79	-	-
			E10/29	8.5	296480	9.74	159	5.62	-	-
			-	-	-	-	160	1.00	-	-
			E11/30b	*	-	-	161	0.0	-	-
September 28	Ferry-Tucson to L.A.	043	F1/-	-	296490	16.33	166	0.0	-	-
			F2/-	-	296500	5.18	167	0.0	-	-
			F3/-	-	-	-	168	3.07	-	-
			-	-	-	-	169	4.22	-	-
			-	-	-	-	170	2.54	-	-
			F4/31	10.7	-	-	171	2.34	-	-
			F5/32	6.2	-	-	172	1.62	-	-
			F6/33	4.9	-	-	173	0.32	-	-
			F7/34	15.6	-	-	174	2.3	-	-
			F8/35b	0.25	-	-	-	-	-	-

[a] Sum of all stages & final filter, no cyclone preceding impactor. The symbol * indicates below detectable levels. The symbol b indicates blank filters.

[b] Used blank of 1.36ug $SO_4^=$/filter. Bendix 240 cyclone (RSP) has 50% aerodynamic diameter cut off ~3um.

[c] Original data using blank of 0.99ug S/filter. TH has aerodynamic cut point ~2um.

[d] Sum of all 8 stages with Bendix 240 cycline (RSP) in front of LPI sampler

[e] Sample contaminated.

Table A3. XRF and PIXE Analyses of the Lundgren Impactor (L II) Final Filters, VISTTA Field Program, September, 1978.

Sample #	$SO_4^=$ ($\mu g/m^3$) XRF	PIXE
C2	2.08	7.45
C3	1.04	*
C5	0.88	*
E3	1.25	2.85
E7	4.90	4.10
E8	26.45	33.77
E9	18.56	19.95
E10	9.16	7.21

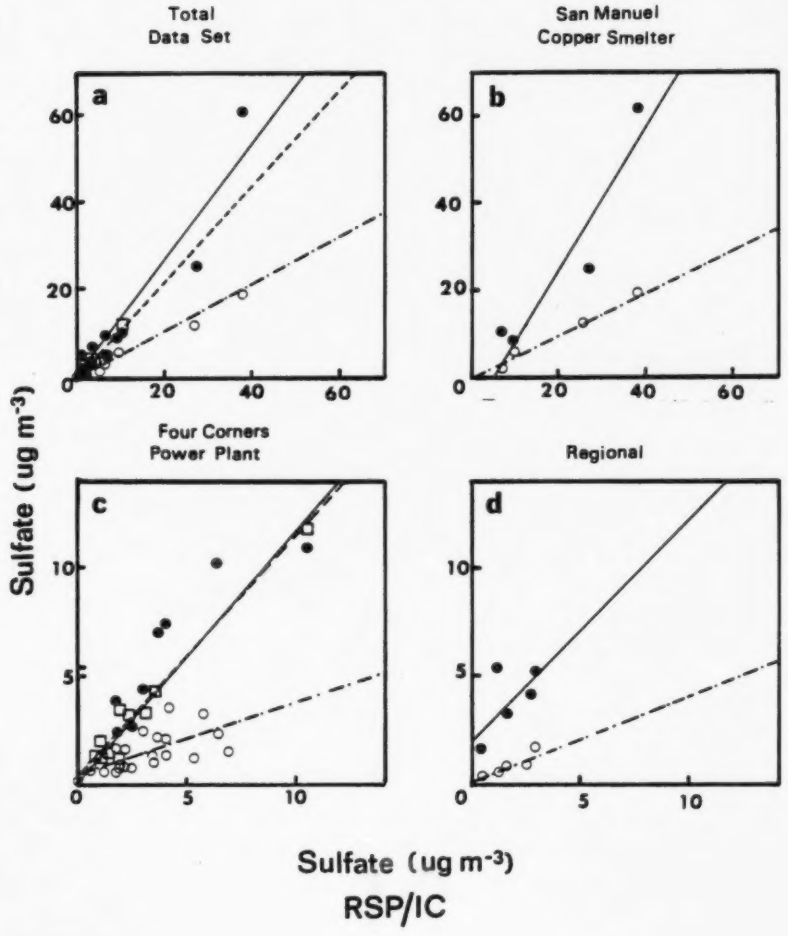


Fig. A1. Intercomparison of sulfur values assumed to be sulfate ($\mu g\ m^{-3}$) with the IC values always plotted on the ordinate. The various slopes, intercepts, correlation coefficients and scattering coefficients (χ^2) are given below.

Total Data Set

	RSP/IC vs.	Slope	Intercept ($\mu gSO_4^{=}/m^3$)	Correlation Coefficient	χ^2	Number of Points
□	LPI/FVFPD[a]	1.09	0.42	0.99	0.23	10
●	LI/PIXE	1.36	0.02	0.95	18	19
○	TN/FVFPD	0.48	0.01	0.98	0.43	35

San Manuel

	RSP/IC vs.	Slope	Intercept ($\mu gSO_4^{=}/m^3$)	Correlation Coefficient	χ^2	Number of Points
●	LI/PIXE	1.69	-9.34	0.96	58.1	4
○	TN/FVFPD	0.51	-1.00	0.99	1.48	4

Four Corners Power Plant

	RSP/IC vs.	Slope	Intercept ($\mu gSO_4^{=}/m^3$)	Correlation Coefficient	χ^2	Number of Points
□	LPI/FVFPD[a]	1.09	0.42	0.99	0.23	10
●	LI/PIXE	1.06	1.23	0.86	2.81	10
○	TN/FVFPD	0.38	0.31	0.73	0.36	22

Regional Flight

	RSP/IC vs.	Slope	Intercept ($\mu gSO_4^{=}/m^3$)	Correlation Coefficient	χ^2	Number of Points
●	LI/PIXE	1.01	2.07	0.65	1.43	5
○	TN/FVFPD	0.41	0.01	0.80	0.09	6

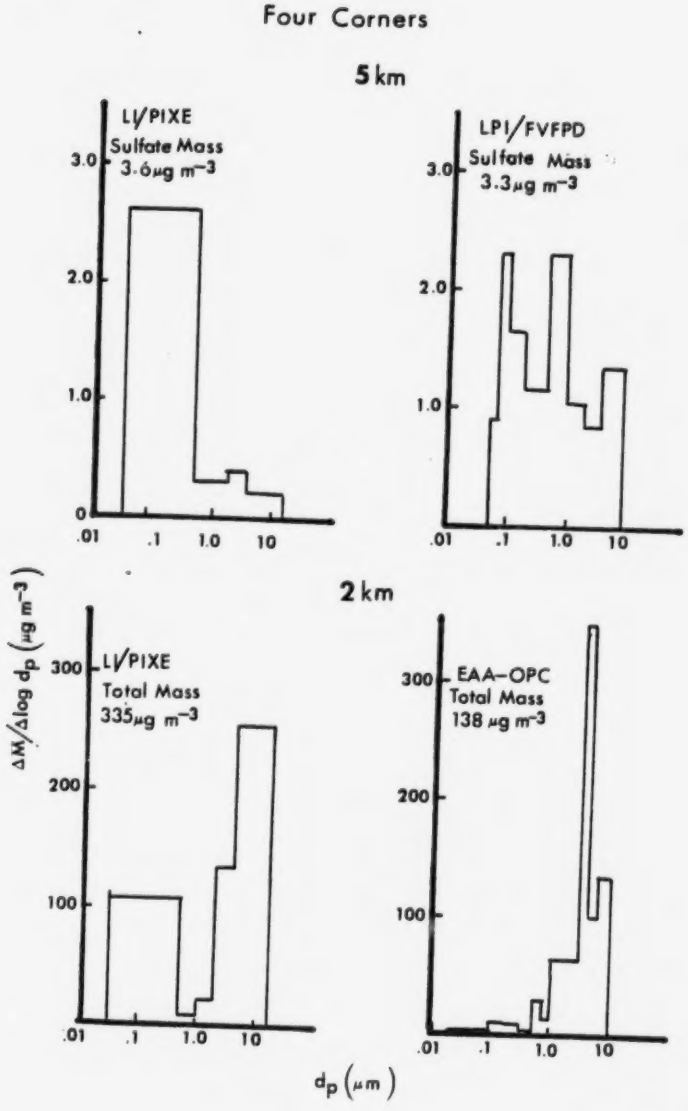
[a]Ground and aircraft data

The very low slope for the comparison of the TM/FVFPD values with the RSP/IC values for all data sets may be at least partly due to a smaller and more efficient cutpoint for the TM sampler. The sampler was run at unusually high flow rates of 26 to 31 ℓ min^{-1} rather than the usual 10 to 15 ℓ min^{-1} for which the cutpoint is 2.5 μm. The effect of cutpoint on measured sulfur concentrations can be seen in Figure A3 where the LPI/FVFPD data for different cutpoints are plotted against the corresponding RSP/IC data. The TM/FVFPD data from the Four Corners power plant are also plotted suggesting that if the TM sampler had a cutpoint between 0.5 and 1 μm the discrepancy could be explained completely. It is likely that unusually high blank sulfur values for the TM/FVFPD analysis is also adding to the discrepancy.

The RSP/IC sulfate concentrations have been used in the analyses of sulfur chemistry in this report because 1) there is excellent agreement between the LPI/FVFPD and the RSP/IC but not among the other data sets, 2) the RSP/IC data are available for all plume orbits while the LPI/FVFPD is available for only 5 orbits, 3) the LI/PIXE data show large scatter for lightly loaded samples, 4) the TM/FVFPD are quite low probably due to a lower than assumed cutpoint and high blank problems, and 5) there is very good correlation between the RSP/IC sulfate values and the b_{sp} values measured with the nephelometer in the region and background (Figure A4).

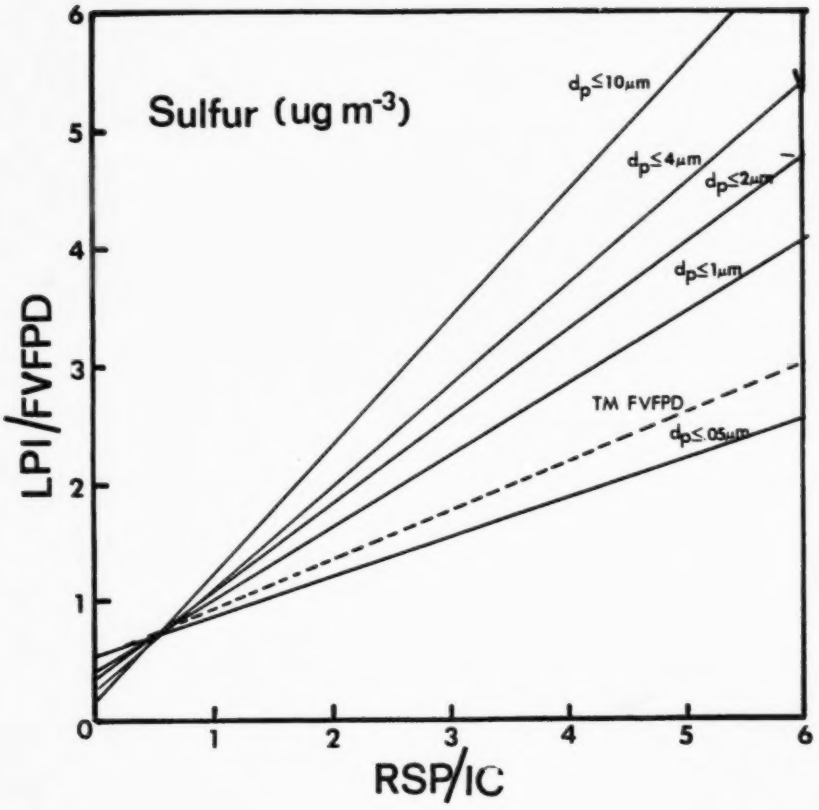
2. SIZE DISTRIBUTIONS.

There seem to be serious problems with all size distribution data from the aircraft for the 1978 VISTTA Field Study except for the LPI/FVFPD sulfur size distributions. As indicated in the previous section the RSP/IC sulfate concentrations all seem quite reasonable. A comparison of these to the total mass calculated from the electrical aerosol analyser (EAA) and optical particle counter (OPC) data using average aerosol densities given in Table A4 shows RSP/IC <u>sulfate</u> values are often nearly equal to the <u>total</u> mass for the background and regional data which indicates that something is wrong with the EAA and OPC data. Total mass from the LI/PIXE data seem reasonable but these are always about a factor of two greater than the EAA-OPC total masses as can be seen in Figure A5 and Table A4. Also, the b_{sp} values from the nephelometer are about a factor of two greater than those calculated using Mie theory from the EAA-OPC data as can be seen in Table A4 and Figure A5. Data used in these calculations are given in Tables A5 and A6. It seems likely that the EAA-OPC data are low by about a factor of 2 perhaps due to a calibration error. Also, there may be significant changes in bin size due to the use of the EAA at altitudes other than sea level (Ogren, 1981). Thus, the EAA-OPC data have not been analyzed in this report.

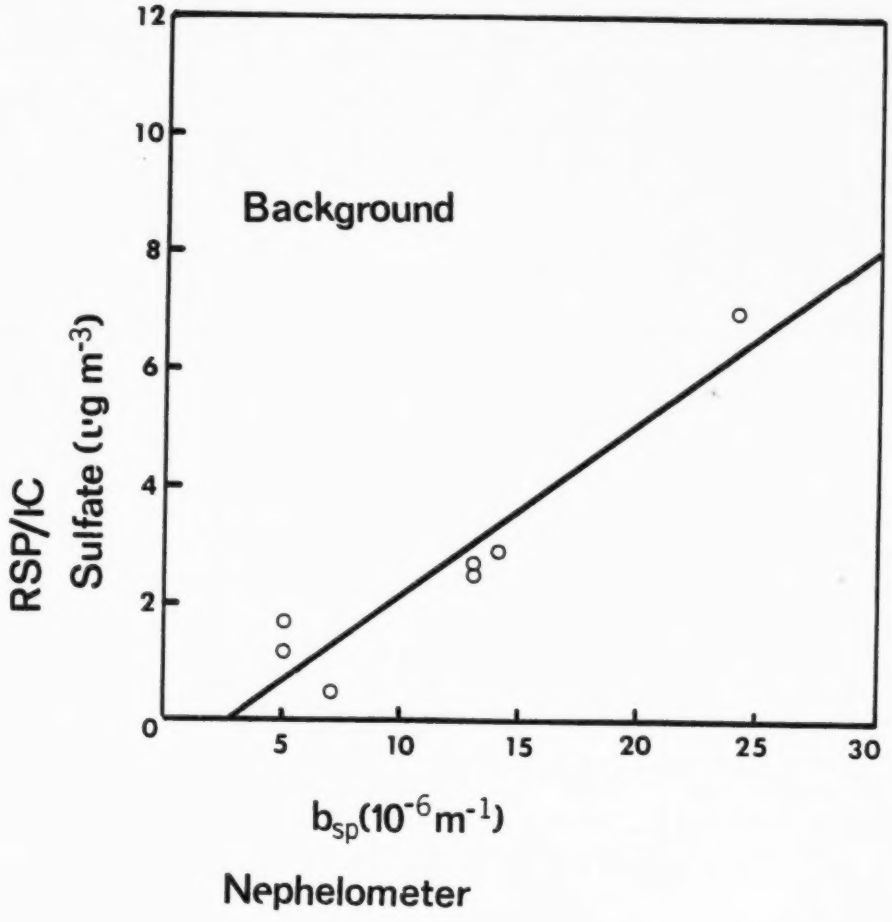


A2a. Comparison of the LI/PIXE and LPI/FVFPD sulfur mass size distributions 5 km downwind of the Four Corners power plant (NM), September 15, 1978. Both are plotted against the aerodynamic diameter.

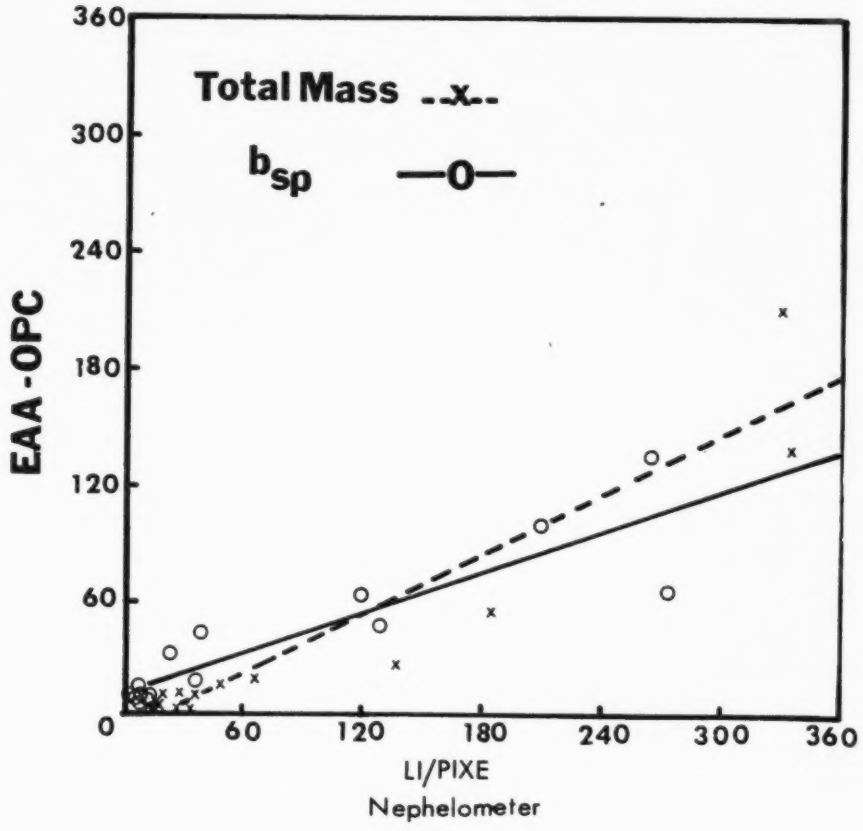
b. Comparison of the LI/PIXE and EAA-OPC total mass size distributions 2 km downwind of the Four Corners power plant September 16, 1978. The PIXE total mass was calculated assuming the chemical composition in Table A5 and is plotted against the aerodynamic diameter.



A3. LPI/FVFPD sulfur values for different aerodynamic cutpoints from <0.5 μm to <10 μm (with the RSP cyclone in front) compared to the corresponding RSP/IC values to show the effect of cutpoint on the slope and intercept. TM/FVFPD data for this day are also plotted. Data are from the Four Corners (NM) power plant, September 15, 1978.



A4. Regression of the RSP/IC sulfate values with the b_{sp} values from the nephelometer for the background and regional flights. The slope is 0.29×10^{6} µg m^{-2}, intercept of -0.77 µg sulfate m^{-3}, $\chi^2 = 0.43$ and correlation coefficient 0.94.



A5. Plot of EAA-OPC b_{sp} and total mass values against the nephelometer b_{sp} values and LI/PIXE total mass values (given in Table A4). September 14 to September 28, 1978.

Table A4 . Comparison of Typical EAA-ROYCO data for September 1978. VISTTA Program.

Date	Distance Downwind (km)	Mass Concentration ($\mu g/m^3$) EAA-ROYCO[a]	LI/PIXE[b]	RSP/IC[c]	$b_{sp}(10^{-6} m^{-1})$ EAA-ROYCO[d]	Nephelometer[e]
	Four Corners					
September 15	5	210	330	14.0	136	266
September 16	2	138	335	8.5	99	211
	12	55	185	7.6	47	130
	34	23	34	5.6	18	37
	Bkg.	2.8	16	2.3	6	5
	Regional					
September 26		11	36	3.9	9	14
		5	26	3.3	8	13
		6	17	2.1	12	8
		2.5	13	0.7	9	7
		4	33	1.6	10	5
		12	28	3.6	15	13
	San Manuel					
September 27	10	27	137	50.9	66	275
	35	21	66	36.0	62	121
	90	17	48	12.9	43	40
	Bkg.	11	19	9.3	32	24

[a] Total EAA-ROYCO mass concentration calculated from average volume concentrations for the orbit assuming a density of 1.7 g/cm^3 for particles <1um geometric diameter and a density of 2.3 for particles between 1 and 17.8 μm.

[b] LI/PIXE total mass concentration was determined from the elemental data for all stages and final filter by assuming the elements were in the form of the compounds listed in Table A6.

[c] These are the RSP/IC concentrations for $(NH_4)_2 SO_4$.

[d] The EAA-ROYCO scattering coefficients were calculated from the volume concentration data from the EAA and ROYCO samplers using the Mie coefficients given in Table A7 for all particles up to 17.8μm geometric diameter.

[e] The nephelometer b_{sp} values are the b_{scat} values of the nephelometer less Rayleigh scattering which was assumed to be $12 \times 10^{-6} m^{-1}$. According to Sverdrup (1977) the nephelometer determines the scattering of particles with geometric diameter <2um at greatly reduced efficiency.

Table A5. Chemical Species and Densities Used in Calculating Total Masses.

Element	Assumed Chemical Species	Conversion Factor[a]	Density (g/cm^3)
Al	Al_2O_3	1.9	2.4
Si	SiO_2	2.1	2.3
S	$(NH_4)_2SO_4$	4.1	1.8
K	K_2O	1.2	2.3
Ca	CaO	1.4	3.3
Ti	TiO_2	1.6	4.3
V	V_2O_3	1.8	4.9
Cr	Cr_2O_3	1.5	5.2
Mn	MnO_2	1.6	4.5
Fe	Fe_2O_3	1.4	5.2
Ni	NiO	1.3	7.5
Cu	CuO	1.3	6.4
Zn	ZnO	1.2	5.5
Pb	PbO	1.1	9.5
	$PbBr_2$	1.8	6.6
	$PbCl_2$	1.3	5.9

Table A6. Values of Aerosol Volume Scattering Efficiency Used to Calculate the Particle Scattering Coefficient Distribution[a]

Particle Size Interval (μm)	$\frac{\Delta b_{sp}}{\Delta V}$ $(10^{-6}{}_m{}^{-1}{}_{\mu m}{}^{-3}{}_{cm}{}^{3})$
0.0056 - 0.01	.0002
0.01 - 0.0178	.0014
0.0178 - 0.0316	.0078
0.0316 - 0.0562	.0440
0.0562 - 0.1	.249
0.1 - 0.178	1.35
0.178 - 0.316	5.20
0.316 - 0.562	10.4
0.562 - 0.75	9.84
0.75 - 1.0	5.66
1.0 - 3.16	2.02
3.16 - 4.22	0.919
4.22 - 5.62	0.176
5.62 - 10	0.5
10 - 17.8	0.25

[a]Mie computations performed using subrontine MIE2, a modified version of subrontine DBMIE developed by J.V. Dave and reported in IBM 360D-17.4.002. Modifications were performed at the University of Washington by D.S. Ensor.